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RESEARCH ARTICLE

REVISED Theoretical structural study of van der Waals complexes between oxazole and atmospheric gases CO_2 and N_2 for capture applications.

[version 4; peer review: 3 approved]

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Abstract

Background

The objective of this study is to explore the potential of Oxazole (Oxa, C_3H_3NO), a fascinating heterocyclic compound naturally present, which is a potential ligand in the construction of Metal-Organic Frameworks (MOFs) for the selective capture of CO_2 in a nitrogen-rich atmosphere, using both molecular and solid-state simulation techniques.

Methods

This study investigates the equilibrium structures and binding energies of van der Waals aggregates formed by an Oxazole molecule with nonpolar molecules such as CO_2 and N_2, considering both two-body systems (Oxazole-CO_2 and Owazole-N_2) and three-body systems

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(Oxazole-CO_2-N_2 and Oxazole-CO_2/N_2-Au_6/Cu_6/Zn_3O_3). Molecular computations for these systems are conducted using ab initio calculations at the MP2/aug-cc-pVXZ level of theory, where X = (D, T). Additionally, solid-state simulations analyze the adsorption behaviors and energies of Oxazole-CO_2 and Oxazole-N_2 on metallic surfaces:Au, Cu and ZnO(111) through Monte Carlo methods.

Results

We find that the Oxazole exhibits more adsorption selectivity for CO_2 than for N_2. Adding a second gas to the most stable complexes, Oxazole-CO_2 and Oxazole-N_2, the Oxazole capture ability does not vary. On the contrary, it strengthens the adsorption energy of three-body complexes compared to two-body complexes. The addition of metallic clusters (Au_6, Cu_6, Zn_3O_3) and metallic surfaces (Au, Cu, ZnO) enhances the adsorption capacity, where Cu_6 is particularly efficient. Both ZnO and Cu surfaces offer significant adsorption advantages while remaining economically feasible.

Conclusions

This study demonstrates that Oxazole exhibits a strong selectivity for CO_2 over N_2, with the addition of metallic clusters and surfaces significantly enhancing its adsorption capacity. These findings highlight the potential of Oxazole-based materials for effective gas capture and separation, with positive implications for environmental sustainability.

Plain language summary

This research project focuses on gas capture and separation, especially for molecules like carbon dioxide (CO_2) and nitrogen (N_2), which are crucial in both industrial and environmental contexts. Metal-organic frameworks (MOFs) show promise for efficient CO_2 capture due to their adjustable structures and large surface areas. However, the use of oxazole, a specific molecule, for CO_2 capture in these structures has been little explored. This study examines how oxazole interacts with CO_2 and N_2 molecules, forming aggregates bound by van der Waals forces (a type of molecular attraction). Results show that oxazole favors binding with CO_2 over nitrogen, making it potentially useful for gas separation. By adding metallic clusters, such as gold, copper, or zinc oxide, the adsorption capacity of oxazole further improves, especially with copper, while remaining affordable.

This study highlights oxazole's potential for effective gas capture, contributing to more sustainable and environmentally friendly technologies.

Keywords

Adsorption, CO2 capture, N2, atmosphere, ab initio, MOF's.

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REVISED **Amendments from Version 3**

In this revised version of the manuscript, a few improvements have been made: the abbreviation "Oxa" for Oxazole has been introduced earlier in the Background and Introduction sections, the sentence regarding open-source software has been rephrased in a neutral tone, the notation has been standardized (Oxa–CO_2, Oxa–N_2) and the units of adsorption loading have been clarified.

Any further responses from the reviewers can be found at the end of the article

Introduction

The exploration of carbon dioxide capture and separation from gas mixtures by adsorption based on porous materials searching for low-cost and high efficiency, has been a focal point in research[1–7], aiming to address environmental concerns and enhance industrial processes[5,6]. Gas adsorption and separation, particularly involving quadrupolar species such as carbon dioxide (CO_2) and nitrogen (N_2), have gained considerable interest due to their importance in industrial and environmental contexts. Metal-organic frameworks (MOFs) are porous crystalline materials formed by organic structures that act as ligands[8] connected by metal ions or clusters[9,10]. They have been considered to be efficient for CO_2 capture tools owing to their adjustable and tunable structures[2], extensive surfaces[11,12], large surface areas[13,14], customizable functionalities[15,16], and high mechanical and thermal stabilities[17]. Specific organic ligands, such as heterocycles like carboxylic acids[18,19], amines[20], imidazoles[21–25], triazoles[26], pyridines[27], benzenes[28], naphthalenes[29], benzimidazoles[30], etc., enable the regulation of (MOFs) properties, thereby enhancing their capability for selective adsorption and thermal stability[31], making them particularly suitable for gas adsorption and separation processes[32]. (MOFs) based on imidazole have gained interest due to the ability to design various types of architectures such as rigid, flexible, interpenetrating, etc., to influence the size of cavity pores and different types of supramolecular interactions within the pore[33,34].

In our previous study[21–24], we highlighted the significant ability of imidazole to form van der Waals complexes with several greenhouse gases, including CO_2, CH_4, and SF_6, as well as with pollutants such as SO_2 and NH_3 and gas such as CO. This interaction is particularly relevant for selectively capturing CO_2 from mixtures containing these gases. Although Oxazole (Oxa, C_3H_3NO) is a fascinating heterocyclic compound naturally present[35], its capacity as a ligand in the construction of CO_2 capturing (MOFs) has not been thoroughly investigated. This provides an opportunity for further research aimed to valorize the properties of Oxazole in developing efficient (MOFs) for CO_2 capture, contributing to advancements in environmental sustainability and gas separation technologies. Our goal is the theoretical characterization of van der Waals aggregates formed with one Oxazole molecule and nonpolar molecules such as carbon dioxide (CO_2) and nitrogen (N_2). CO_2 is known to have significant environmental impacts on global weather patterns and human life[36]. Anthropogenic emissions of N_2 can indirectly lead to an increase in NO_x levels in the atmosphere. When N_2 reacts with atmospheric oxygen, it converts into nitrogen oxides (NO_x) such as NO and NO_2. These NO_x compounds have consequences on air quality, human health, and the environment, contributing to smog formation, acid rain, and causing harmful effects on respiratory systems and lung tissues[37].

In this work, we perform a systematic evaluation of ligands containing both nitrogen and oxygen for their interaction energies with CO_2 and N_2 by using both molecular and solid-state simulation techniques. In the first approach, we use the possible accurate ab initio methods to calculate the binding energies (BEs) of the two body systems (CO_2-Oxa-BEs & N_2-Oxa-BEs). The analysis of the ternary systems (CO_2-Oxa-N_2-BEs) and (Oxa-CO_2/N_2-Au_6/Cu_6/Zn_3O_3) using the same method was conducted to understand the interactions among CO_2, Oxazole, and N_2 within these systems, to examine their influence on CO_2 separation and capture strategies in gas mixtures, and predict the capacity of new materials to selectively capture and store CO_2 over N_2 in N_2-rich atmospheres. Indeed, the presence of N_2 can significantly influence CO_2 capture performance in (MOFs), taking into account their common presence in atmospheric and industrial environments, emphasizing the crucial role of computational methods in designing nanomaterials for carbon capture technologies.

On the other hand, the Monte Carlo solid-state simulations were employed to investigate the interactions between Oxazole and the (111) surfaces of Au, Cu, and ZnO. These materials were selected for their unique electronic properties and practical relevance. Gold (Au) is frequently used as a reference due to its stability and well-characterized surface chemistry[38], Copper (Cu) is chosen for its economic viability and its proven effectiveness in enhancing adsorption processes[39]. While zinc oxide ZnO was included in this study for its unique semiconducting, piezoelectric, and photoelectric properties and high surface area[40].

Computational details

All the electronic computations were performed using the Gaussian 09 Revision C.01[41] and MOLPRO[42], as well as the Material Studio (BIOVIA, 2020) program[43]. An appropriate free alternative software for this purpose is GAMESS (US), a powerful tool for electronic structure calculations that supports HF, DFT, MP2, and other methods, and ORCA, a versatile quantum chemistry program renowned for its computational efficiency and support for DFT, HF, and post-HF techniques.

We have combined the most accurate possible ab initio method, and Monte Carlo solid-state simulations[44], to investigate the interaction between CO_2 and N_2 and Oxazole (Oxa), either isolated, attached to gold, copper and ZnO cluster or surface.

The study employed the second-order Møller–Plesset theory (MP2)[45,46] within the Gaussian software to compute the equilibrium structures and spectroscopic properties of both isolated species and complexes included two-body systems like Oxa-CO_2 and Oxa-N_2. Additionally, the three-body systems such as Oxa-CO_2-N_2 and Oxa-CO_2/N_2-Au_6/Cu_6/Zn_3O_3 were investigated. For an accurate depiction of small systems, in these computations, the atoms were described using Dunning and co-workers' aug-cc-pVXZ basis set (abbreviated as AVXZ, where X=D, T)[47], augmented with diffuse atomic orbitals to capture long-range interactions. Specifically, AVTZ was employed for Oxa-CO_2 and Oxa-N_2, while AVDZ was used for Oxa-CO_2-N_2 and Oxa-CO_2/N_2- cluster complexes.

Monte Carlo (MC) simulation[48] is a widely used computational method for investigating molecular adsorption on surfaces, particularly for estimating adsorption energies (E_{ads}) and modeling adsorption isotherms. Based on the Metropolis algorithm[49], it explores configurational space by evaluating randomly generated molecular states according to energy changes and thermodynamic probability. In this study, the Adsorption Locator module, implemented in Materials Studio 2020 (BIOVIA)[43], was employed in conjunction with the COMPASS II force field[50] to examine the adsorption energies of Oxa-N_2, and Oxa-CO_2 on gold, copper, and zinc oxide surfaces. Atomistic grand canonical Monte Carlo (GCMC) simulations were performed to estimate the adsorption isotherms of Oxa-CO_2 and Oxa-N_2 on Au (111), Cu (111), and ZnO (111) surface.

As a free alternative to Material Studio, the open-source software packages Quantum ESPRESSO and CP2K. The first program, Quantum ESPRESSO, is a comprehensive suite for quantum simulations, ideal for materials modeling and the simulation of solids, liquids, and nanostructures.

https://www.quantum-espresso.org/

The second program, CP2K, is also free and open-source software, widely used for molecular dynamics simulations and quantum chemistry calculations, particularly for systems with large numbers of atoms.

https://www.cp2k.org/

The Au, Cu, and ZnO crystal structures have been imported from the Materials Studio database. Surfaces were built by clicking 'Build', then 'Surface', and then 'Cleave Surface'. In the following menu, the cleaving plane (1 1 1) was chosen, and then afterward, the 'Symmetry' option was used to construct a supercell. All the surface structures were prepared with three layers, as illustrated in Figure 5.

The structures of Oxazole, Oxa-N_2, and Oxa-CO_2 were optimized to obtain their lowest-energy configurations using the COMPASS II force field, as implemented in the Forcite Module. This same force field was used in the Monte Carlo simulations. The simulations were done utilizing the Adsorption Locator Module in the Materials Studio 2020 package from BIOVIA. These simulations involved 10 cycles of 10,000 steps each, providing insights into adsorption processes relevant to catalysis, materials science, and environmental applications.

Therefore, a detailed investigation of adsorption behaviors and energies of the fixed molecules on the chosen surfaces provides valuable insight into their eventual interactions and stability.

The minimum character of all the optimized structures is evidenced by the presence of all positive harmonic frequencies, indicating that the system is at its energy minimum, reflecting a stable and optimized configuration. The binding energy (BE) between Oxazole and CO_2 or N_2 was initialy evaluated for optimized geometries using Second-order Møller-Plesset perturbation theory (MP2) in connection with aug-cc-pVTZ basis set (denoted in this paper by AVTZ). To confirm the accuracy of MP2, single-point energy calculations were subsequently performed on the MP2 geometries using the explicitly correlated coupled cluster method, CCSD(T)-F12b[51,52], as implemented in MOLPRO[42], in combination with the AVTZ orbital basis set. The default auxiliary basis sets AVnZ/MP2FIT and VnZ/JKFIT were employed for density fitting (DF) and resolution of the identity (RI), respectively. The binding energies (BEs) were calculated using the following energy expression:

$$BE = E_{Complex} - (E_{Oxazole} + E_{gaz})$$

where: BE is the binding energy, $E_{complex}$ is the total energy of the Oxazole-gas complex, $E_{Oxazole}$ is the total energy of the isolated Oxazole molecule, and E_{gaz} is the total energy of the isolated gas molecule (CO_2 or N_2). For a more accurate estimation of the interaction energy, the basis set superposition error (BSSE) was corrected using the Boys and Bernardi method[53]. Additionally, the zero-point vibrational energy correction (ZPVE) was also taken into account for all geometries[54].

For the complexes between Oxazole and CO_2 or N_2 - cluster (Au_6, Cu_6 or Zn_3O_3) we employed the MP2 method with aug-cc-pVDZ for non-metals and LANL2DZ ECP[55] for metals, and for the adsorption of CO_2 and N_2 on Au, Cu, and ZnO (111) surfaces, we used the Monte Carlo computational technique.

The binding energies (BEs) were calculated using the following energy expression:

$$BE = E_{Complex} - (E_{Oxa\text{-}CO_2/N_2} + E_{Cluster/Surface})$$

where: BE is the binding energy $E_{complex}$, is the total energy of the Oxa-CO_2/N_2-cluster (cluster = Au_6/Cu_6 or Zn_3O_3) or Surface Au, Cu or ZnO (111) complexes, $E_{Oxa\text{-}CO_2/N_2}$ is the total energy of the complex Oxa+CO_2 or Oxa+N_2, and $E_{Cluster/Surface}$ is the total energy of the isolated gas cluster (Au_6, Cu_6 or Zn_3O_3) or Surface Au(111), Cu (111) or ZnO (111). For a more accurate estimation of the interaction energy of Oxa-CO_2/N_2-cluster (cluster= Au_6/Cu_6 or Zn_3O_3) the zero-point vibrational energy correction (ZPVE) was also taken into account for all geometries.

Results and discussions

Equilibrium structure of the complexes

To examine the molecular-level adsorption of CO_2 and N_2 on Oxazole, we first located the CO_2 and N_2 molecules at the N1 site of Oxazole (refer to Figure 1) and then we oriented them around it to explore all possible equilibrium structures. It's worth noting that the number of stable structures increases the likelihood of gas capture. Despite multiple attempts, the optimization results at the MP2/AVTZ level consistently converged toward one of the structures presented in Figure 1A and 1B, which characterize the complexes formed by Oxazole with CO_2 and N_2.

The study carried out at the MP2/AVTZ level on the Oxa-CO_2 complex reveals the existence of two stable structures labeled I1 and I2 (cf. Figure 2A, Table 1). In structure I1 (E_r = 0.0 kcal/mol), identified as the global minimum, the bond is established through an interaction between the electron

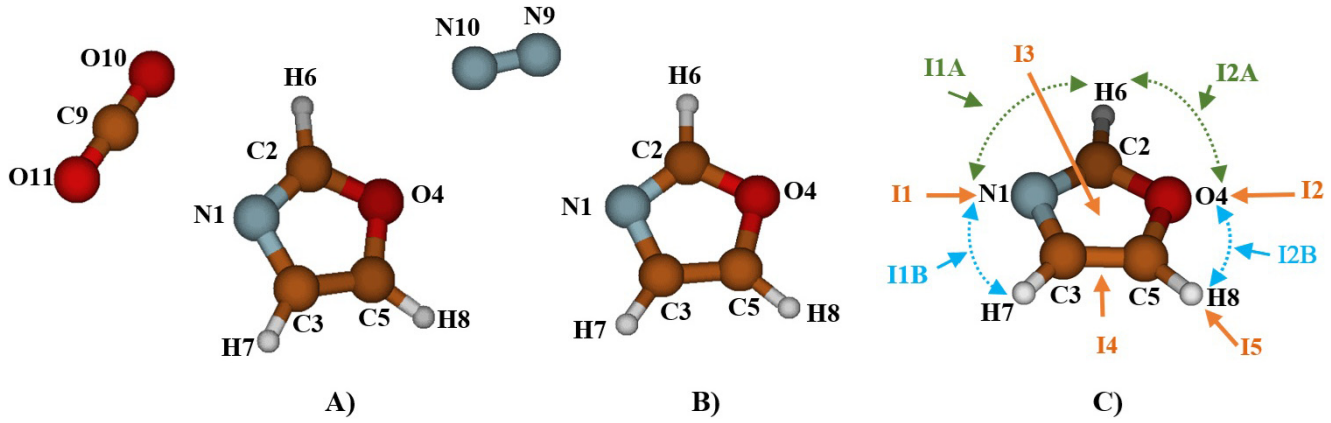

Figure 1. The atom labeling of the complex Oxazole + CO_2 (**A**), Oxazole + N_2 (**B**) and Oxazole and the five principal complexation pathways, I1, I2, I3, I4, and I5 (**C**).

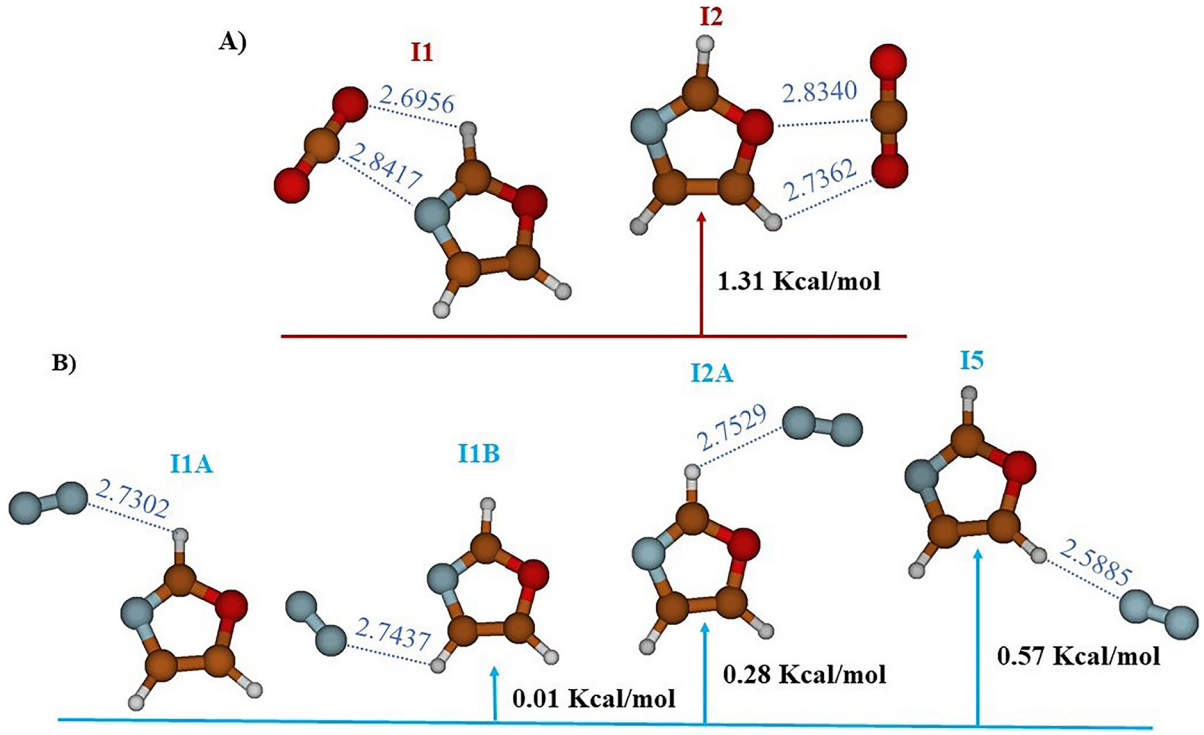

Figure 2. The equilibrium geometries and the MP2/AVTZ relative energies of the Oxazole +CO_2 (**A**) and Oxazole + N_2 (**B**) Van der Waals complexes.

Table 1. Total electronic energies (E, in a.u.), relative energies (E_r, in kcal/mol) and structural parameters (Distances in Å; angles in degrees) of the two equilibrium structures of the Oxa-CO_2 complexes calculated with MP2/aug-cc-pVTZ.

Oxazole (C1)		I1 (C1)		I2 (C1)	
		ROH / RCN	2.6956 / 2.8418	ROH / RCO	2.7362 / 2.8340
E	-245.639836	E	-433.968056	E	-433.965972
		E_r	0.0	E_r	1.31
C2N1	*1.2996*	*C2N1*	*1.3011*	*C2N1*	*1.2987*
C3N1	*1.3862*	*C3N1*	*1.3858*	*C3N1*	*1.3869*
O4C2	*1.3552*	*O4C2*	*1.3531*	*O4C2*	*1.3570*
C5C3	*1.3596*	*C5C3*	*1.3597*	*C5C3*	*1.3593*
H6C2	*1.0755*	*H6C2*	*1.0757*	*H6C2*	*1.0757*
H7C3	*1.0752*	*H7C3*	*1.0752*	*H7C3*	*1.0752*
H8C5	*1.0739*	*H8N4*	*1.0739*	*H8N4*	*1.0741*
C3N1C2	*104.0*	*C3N1C2*	*104.2*	*C3N1C2*	*104.1*
O4C2N1	*114.7*	*O4C2N1*	*114.5*	*O4C2N1*	*114.6*
C5C3N1	*109.1*	*C5C3N1*	*109.0*	*C5C3N1*	*109.3*
H6C2N1	*128.6*	*H6C2N1*	*128.2*	*H6C2N1*	*128.8*
H7C3N1	*122.1*	*H7C3N1*	*122.1*	*H7C3N1*	*122.0*
H8C5O4	*116.7*	*H8C5O4*	*116.8*	*H8C5O4*	*116.6*
	CO_2				
E	-188.321641				
CO	*1.1702*	*O10C9*	*1.1718*	*O10C9*	*1.1709*
		O11C9	*1.1686*	*O11C9*	*1.1690*
<OCO	*180.0*	*<OCO*	*177.6*	*<OCO*	*179.3*
		O10H6	*2.6956*	*O10H8*	*2.7362*
		O10H6C2	*104.2*	*O10H8C5*	*111.2*
		C9O10H6	*114.7*	*C9O10H8*	*113.6*
		C9N1	*2.8418*	*C9O4*	*2.8340*
		C9N1C2	*106.8*	*C9O4C2*	*142.8*
		O10C9N1	*86.1*	*O10C9O4*	*85.8*

donor-acceptor (EDA) sites of CO_2 and Oxazole (RO10-H6 = 2.6956 Å and RC9-N1 = 2.8418 Å). However, in structure I2 (E_r = 1.31 kcal/mol), the bond is maintained through a donor-acceptor electron exchange (EDA), where the oxygen atom of CO_2 interacts with H8 of Oxazole (RO10H8 = 2.7362 Å) and the carbon atom of CO_2 interacts with the oxygen of Oxazole (RC9-O4 = 2.8340 Å).

Additionally, the study of the complex between N_2 and Oxazole, still at the MP2/AVTZ level, revealed the existence of four adsorption sites as outlined in Figure 2B and Table 3. These sites are labeled as follows: I1A (E_r = 0.0 kcal/mol), I1B (E_r = 0.01 kcal/mol), I2A (E_r = 0.28 kcal/mol), and I5 (E_r = 0.57 kcal/mol). These distinct structures depict various stable configurations of the Oxa-N_2 complex. Predominantly, the key interactions observed in the stable structures occur where hydrogen bonds link N_2 to Oxazole. Additionally, the equilibrium distances within the van der Waals systems RN9Hx (X=6,7,8) exhibit the following variations: RN9H6 = 2.7302 Å for I1A, RN9H7 = 2.7437 Å for I1B, RN9H6 = 2.7529 Å for I2A, and RN9H8 = 2.5885 Å for I5.

Table 1 and Table 3 present the structural parameters at the MP2/AVTZ level, while Table 2 and Table 4 provide the

Table 2. Harmonic fundamental frequencies (ω, in *cm*$^{-1}$) of CO_2, Oxazole, and the two equilibrium geometries of the Oxa-CO_2 complexes calculated at the MP2/AVTZ level of theory.

	Ω							
	Oxazole		***CO_2***		***I1***		***I2***	
ω_1	a	3330			a	3331	a	3330
ω_2		3311				3312		3309
ω_3		3299				3300		3299
ω_4			σ_u	2402		2402		2404
ω_5		1546				1546		1547
ω_6		1508				1506		1507
ω_7		1355				1355		1354
ω_8			σ_g	1326		1327		1328
ω_9		1272				1269		1270
ω_{10}		1185				1189		1182
ω_{11}		1141				1144		1138
ω_{12}		1109				1111		1108
ω_{13}		1086				1086		1082
ω_{14}		915				917		917
ω_{15}		905				909		904
ω_{16}		864				865		868
ω_{17}		827				836		827
ω_{18}		763				766		771
ω_{19}		665				667		664
ω_{20}			π	659		662		660
ω_{21}			π	659		637		651
ω_{22}		628				628		626
ω_{23}						132		100
ω_{24}						88		80
ω_{25}						52		39
ω_{26}						44		38
ω_{27}						29		21

MP2/AVTZ harmonic frequencies for each examined complex. The parameters of the van der Waals aggregates are compared to those of the corresponding isolated components.

During the formation of weak intramolecular bonds, the structure of the Oxazole ring and N_2 undergoes minimal changes (see Table 1 and Table 3). However, a significant deformation is observed in the CO_2 molecule, resulting in the loss of its symmetry. This deformation is particularly pronounced in the Oxa-CO_2 complexes I1 and I2 (see Table 1), where the C-O bond in CO_2 tends to shorten (O11C9: 1.1686 Å for I1, 1.1690 Å for I2), while the distance O10C9 is elongated (1.1718 Å for I1, 1.1709 Å for I2), compared to free CO_2 (CO=1.1702 Å). Additionally, the <OCO angle is bent away from the linear configuration of a free CO_2 molecule, measuring 177.6 degrees for I1 and 179.3 degrees for I2, respectively. This deformation is attributed to the formation of the van der Waals complexes between CO_2 and Oxazole, leading to electron redistribution and strengthening of the C-O bond.

Harmonic frequencies were computed to ensure minimal energy for all structures. Notably, in Table 2 and Table 4, certain low frequencies (5 frequencies for Oxa-CO_2, ω_{23}-ω_{27}, and for Oxa-N_2, ω_{20}-ω_{24}) emerge, which were not observed for the monomers. This situation allows for the use of a Born-Oppenheimer-type approach, which distinguishes between intramolecular and intermolecular vibrations. Intermolecular vibrations more closely resemble hindered rotations or tunneling motions. Generally, there is a strong coupling between different intermolecular degrees of freedom. The deformation vibrations of O–C–O in complexes I1 and I2 occur at frequencies of 637 cm^{-1} and 651 cm^{-1}, respectively. These modes experience significant frequency shifts compared to the CO_2 monomer, approximately 8 cm^{-1} for complex I2 an 22 cm^{-1} for complex I1. Furthermore, the symmetric and antisymmetric intermolecular O-C stretching modes with frequencies ω_8 = 1328 cm^{-1} and ω_4 = 2402 cm^{-1} for complex I2 have shifted by 2 cm^{-1} from frequencies of ω_8 = 1326 cm^{-1} and ω_4 = 2404 cm^{-1} for the CO_2 monomer. In the Oxa-N_2 complex, the stretching mode of N-N is not influenced by the formation of the hydrogen bond between the N of N_2 and the H of Oxazole. Thus, the intermolecular stretching vibrations H..N–N(ω_{21}) in the optimal structure are observed at frequencies of 63 cm^{-1}, 58 cm^{-1}, 54 cm^{-1}, and 57 cm^{-1} for I1A, I1B, I2A, and I5, respectively.

Binding energies

Two body complexes type Oxa-CO_2 and Oxa-N_2

The binding energy is crucial for understanding, predicting, and enhancing the performance of adsorbent materials in greenhouse gas and pollutant capture processes. It determines the interaction between the host and the guest, as well as the properties of the adsorbent material. A more negative adsorption energy generally indicates a stronger adsorption interaction. For this reason, the binding energies of all previously mentioned stable forms, are computed via the MP2/AVTZ approach and including the zero-point vibrational energy (ZPVE) along with as well as the Boys and Bernardi correction (BSSE), are listed in Table 5. Our calculations indicate that Oxazole is energetically favored as an adsorbent for both our adsorbates although CO_2 shows a higher capacity to bind Oxazole rings. The range of CO_2 binding energies spans from -4.13 to -2.82 kcal/mol, while for N_2, the energies range from -1.77 to -1.19 kcal/mol. Based on the adsorption energies, the nitrogen site of the Oxazole is the most stable site for CO_2 adsorption, and H6 is the most stable site

Table 3. Total electronic energies (E, in a.u.), relative energies (E_r, in kcal/mol) and structural parameters (Distances in Å; angles in degrees) of the four equilibrium structures of the Oxa-N_2 complex calculated with MP2/aug-cc-pVTZ.

Oxazole (C1)		I1A (C1)		I1B (C1)		I2A (C1)		I5 (C1)	
		R_{NH}	2.7302	R_{NH}	2.7437	R_{NH}	2.7529	R_{NH}	2.5885
E	-245.639836	E	-355.007379	E	-355.007363	E	-355.006923	E	-355.006474
		E_r	0.0	E_r	0.01	E_r	0.28	E_r	0.57
C2N1	2.9962	*C2N1*	1.3003	*C2N1*	1.30006	*C2N1*	1.2997	*C2N1*	1.2998
C3N1	1.38622	*C3N1*	1.3860	*C3N1*	1.3867	*C3N1*	1.3859	*C3N1*	1.3863
O4C2	1.35519	*O4C2*	1.3549	*O4C2*	1.3547	*O4C2*	1.3565	*O4C2*	1.3550
C5C3	1.35957	*C5C3*	1.3597	*C5C3*	1.3597	*C5C3*	1.3597	*C5C3*	1.3599
H6C2	1.07554	*H6C2*	1.0754	*H6C2*	1.0756	*H6C2*	1.0752	*H6C2*	1.0755
H7C3	1.07521	*H7C3*	1.0752	*H7C3*	1.0751	*H7C3*	1.0752	*H7C3*	1.0752
H8C5	1.07390	*H8C5*	1.0739	*H8C5*	1.07388	*H8C5*	1.0733	*H8C5*	1.0738
C3N1C2	103.99	*C3N1C2*	104.0	*C3N1C2*	104.0	*C3N1C2*	104.0	*C3N1C2*	104.0
O4C2N1	114.70	*O4C2N1*	114.7	*O4C2N1*	114.7	*O4C2N1*	114.6	*O4C2N1*	114.7
C5C3N1	109.13	*C5C3N1*	109.1	*C5C3N1*	109.1	*C5C3N1*	109.1	*C5C3N1*	109.2
H6C2N1	128.59	*H6C2N1*	128.4	*H6C2N1*	128.6	*H6C2N1*	128.8	*H6C2N1*	128.7
H7C3N1	122.09	*H7C3N1*	122.1	*H7C3N1*	122.0	*H7C3N1*	122.1	*H7C3N1*	122.0
H8C5O4	116.75	*H8C5O4*	116.9	*H8C5O4*	116.8	*H8C5O4*	116.8	*H8C5O4*	116.7
	N_2								
E	-109.364800								
NN	*1.11401*	NN	1.11387		1.11408		1.11396		1.11401
		N9H6	2.7302	N9H7	2.7437	N9H6	2.7529	N9H8	2.5885
		N9H6C2	109.2	N9H7C3	113.3	N9H6C2	114.9	N9H8C5	167.7
		N10N9H6	147.3	N10N9H7	144.1	N10N9H6	114.9	N10N9H8	172.1

for N_2 adsorption. The zero-point vibrational energy (ZPVE) correction ranges from 0.39 to 0.51 kcal/mol for the CO_2 complexes and from 0.32 to 0.39 kcal/mol for the N_2 complexes. On the other hand, the BSSE correction is between 0.02 and 0.09 kcal/mol for CO_2 and 0.05 kcal/mol for N_2.

Single-point CCSD(T)-F12/AVTZ-F12 calculations were also performed to provide accurate reference values for the interaction energies of the Oxa-CO_2 and Oxa-N_2 complexes. In comparison, the MP2/AVTZ method predicts interaction energies close to these reference values, with deviations of approximately - 0.18 kcal/mol for Oxa-CO_2 and ranging from - 0.41 to - 0.58 kcal/mol for Oxa-N_2.

Three body complexes type CO_2-Oxa-N_2

Since this article focuses on the CO_2 separation properties relative to N_2, the most abundant gas in Earth's atmosphere (78.084%)[56], our aim is to understand, at the molecular level, whether Oxazole-based (MOFs) can simultaneously capture two different gases and how the CO_2 capture capacity varies in the presence of N_2, which a third body can alter the interaction between two bodies. To achieve this, we performed geometry optimizations on three-body systems, namely N_2-Oxa-CO_2, starting from various configurations where CO_2 and N_2 occupy the equilibrium positions of the two-body systems, Oxa-CO_2 and Oxa-N_2. We then examined the capture of the second gas. The resulting structures are presented in Table 6 and illustrated in Figure 3. In Figure 3A, the equilibrium structures of three systems are shown, obtained using the equilibrium configurations of the Oxa-CO_2 complex and rotating N_2 around Oxazole. However, in Figure 3B, the equilibrium structures of three other systems are displayed, obtained using the equilibrium configurations of the Oxa-N_2 complex and rotating CO_2 around Oxazole. The structures in Figure 3A are identified by the symbol "InIm," where "In" and "Im" respectively represent the main complexation

Table 4. **Harmonic fundamental frequencies (ω, in cm^{-1}) of N_2, Oxazole and the four equilibrium geometries of the Oxa-N_2 complexes calculated at the MP2/AVTZ level.**

	Ω											
	Oxazole		***N_2***		***I1A***		***I1B***		***I2A***		***I5***	
ω_1	a	3330			a	3330	a	3330	a	3329	a	3336
ω_2		3310				3314		3310		3316		3310
ω_3		3298				3298		3301		3298		3299
ω_4			σ_g	2187		2186		2185		2186		2186
ω_5		1545				1544		1545		1545		1546
ω_6		1507				1506		1507		1506		1508
ω_7		1355				1354		1354		1355		1356
ω_8		1271				1271		1271		1271		1273
ω_9		1185				1186		1186		1182		1186
ω_{10}		1141				1142		1140		1141		1141
ω_{11}		1109				1109		1110		1108		1113
ω_{12}		1085				1086		1086		1085		1085
ω_{13}		915				914		915		914		915
ω_{14}		904				905		904		904		905
ω_{15}		863				864		870		865		866
ω_{16}		826				834		827		833		827
ω_{17}		763				765		764		763		784
ω_{18}		664				666		665		665		665
ω_{19}		627				628		628		627		630
ω_{20}						84		82		77		58
ω_{21}						**63**		**58**		**54**		**57**
ω_{22}						46		46		42		49
ω_{23}						40		43		26		22
ω_{24}						21		20		13		9

Table 5. **Binding energies of the Oxazole complexes (E_b, kcal/mol).**

Complex	E_{int} (MP2/AVTZ)	E_{int} (CCSD(T)F12/ AVTZ-F12)	E_{int} +BSSE (MP2/AVTZ)	E_{int} +ZPVE (MP2/AVTZ)	E_{int} +BSSE +ZPVE (MP2/AVTZ)
Oxa-CO_2					
I1	-4.13	-3.96	-4.22	-3.62	-3.71
I2	-2.82	-2.64	-2.84	-2.43	-2.45
Oxa-N_2					
I1A	-1.77	-1.19	-1.72	-1.38	-1.33
I1B	-1.76	-1.25	-1.71	-1.39	-1.37
I2A	-1.48	-1.01	-1.43	-1.16	-1.11
I5	-1.19	-0.78	-1.14	-0.85	-0.8

pathways (I1, I2, I3, I4, and I5) of CO_2 and N_2 with Oxazole (Figure 1C), while in Figure 3B, they are identified by the symbol "ImIn". The binding energies in Table 6 are determined by combining the AVDZ basis set with MP2 correlation, which is an appropriate method for three-body systems. We opted for AVDZ over AVTZ due to the size of the systems, which makes the use of AVTZ impossible. These values are then compared to those of two-body complexes (Oxazole+X, where X= CO_2, N_2) calculated using the same level of theory. It is observed that the presence of a second gas appears to be beneficial, thereby enhancing the Oxazole's ability to capture both CO_2 and N_2 without causing competition.

The interaction energies of the three-body systems increase and are higher than those observed in the two-body Oxazole + CO_2 complexes. In the case of the Oxa-N_2+CO_2 complexes, the binding energy ranges between -3.60 kcal/mol and -5.03 kcal/mol, compared to the two-body systems, Oxazole+N_2, whose binding energies are respectively between -1.40 kcal/mol and -1.94 kcal/mol. So, for the Oxa-CO_2+N_2 complexes, the binding energy ranges between -5.94 kcal/mol and -8.40 kcal/mol, compared to the two-body systems Oxa+CO_2, which exhibit binding energies ranging from -3.13 kcal/mol to -4.48 kcal/mol. This is explained by the formation of an additional intramolecular bond between the molecules of the three systems (π-stacking and Van der Waals interactions), which can stabilize the systems. The inclusion of the ZPVE vibrational correction results in a decrease in the energy quantities of three systems, ranging from -0.49 kcal/mol to -1.09 kcal/mol.

Oxa-Au_6, Cu_6 and Zn_3O_3 and CO_2/N_2–Oxa-Au_6, Cu_6 and Zn_3O_3

Recently, various technologies have emerged for CO_2 capture, utilizing methods such as chemisorption and physisorption, due to the development of nanodevices such as metal nanoclusters and metal oxide nanoclusters[57]. These nanocomposite materials have found wide-ranging applications, including energy storage[58], drug delivery[59], and the adsorptive removal of diverse pollutants from contaminated environments[60]. These applications benefit from the materials' high stability, ease of synthesis, and ability to be modulated into various shapes and sizes. This section examines the adsorption and activation of CO_2 and N_2 on small metal clusters (Au_6, Cu_6) and on the metal oxide cluster Zn_3O_3. Even-numbered clusters were chosen because they tend to be more stable and have larger HOMO–LUMO gaps[61–63], ensuring reliable structures during adsorption studies. Moreover, these clusters exhibit a rapid increase in binding energies with increasing cluster size. Notably, these nanoparticles possess the ability to bind with various biological or medicinal molecules containing relevant heteroatoms like nitrogen and oxygen, all while exhibiting low toxicity[64]. The CO_2/N_2–Oxa-Au_6, Cu_6, or Zn_3O_3 complexes were initially formed by attaching the stable structures of two distinct complexes, namely I1 (Oxa- CO_2) and I1A (Oxa- N_2), to the most stable form of Au_6, Cu_6, and Zn_3O_3 (a planar triangle with D3h symmetry), using electron-rich positions such as N[62,63,65,66]. Harmonic vibration frequencies were also calculated at the same theoretical level to identify the obtained structures as local minima. Figure 4 displays the optimized structures for Oxa-Au_6, Cu_6 and Zn_3O_3 and for CO_2/N_2–Oxa-Au_6, Cu_6 and Zn_3O_3. This figure shows that in the Oxazole-cluster structure, the gold, copper, or zinc atoms situated at the apex of the octahedron form a covalent bond interaction at the O4 positions of the Oxazole molecule. As seen in Figure 4, both gases are physically adsorbed, and the I1 and I1A structures of the Oxa-CO_2 and Oxa-N_2 complexes are moderately perturbed by the presence of the cluster. Consequently, in the structure I1-Au_6 and I1-Cu_6, the hydrogen bond between the oxygen

Table 6. MP2/AVDZ binding energies of the two-body and three-body complexes (E_b, kcal/mol).

Complex	E_{int}	E_{int} +ZPVE	Complex	E_{int}	E_{int} +ZPVE
Oxa-CO_2			**Oxa-CO_2+N_2**		
I1	-4.48	-3.95	**I1I5**	-5.94	-5.13
I2	-3.13	-2.74	**I1I2A**	-6.18	-5.40
			I1AI2B	-6.23	-5.44
			I1AI2B	-6.57	-5.70
			I1AI1A	-6.57	-5.71
			I1AI3	-8.40	-7.31
Oxa-N_2			**Oxa-N_2 +CO_2**		
I1A	-1.91	-1.51	**I1AI1A**	-4.85	-4.09
I1B	-1.94	-1.56	**I1A I4**	-3.93	-3.26
I2A	-1.61	-1.28	**I1B I4**	-4.81	-3.98
I5	-1.40	-1.03	**I2A I4**	-3.60	-2.99
			I1B I2	-5.03	-4.354

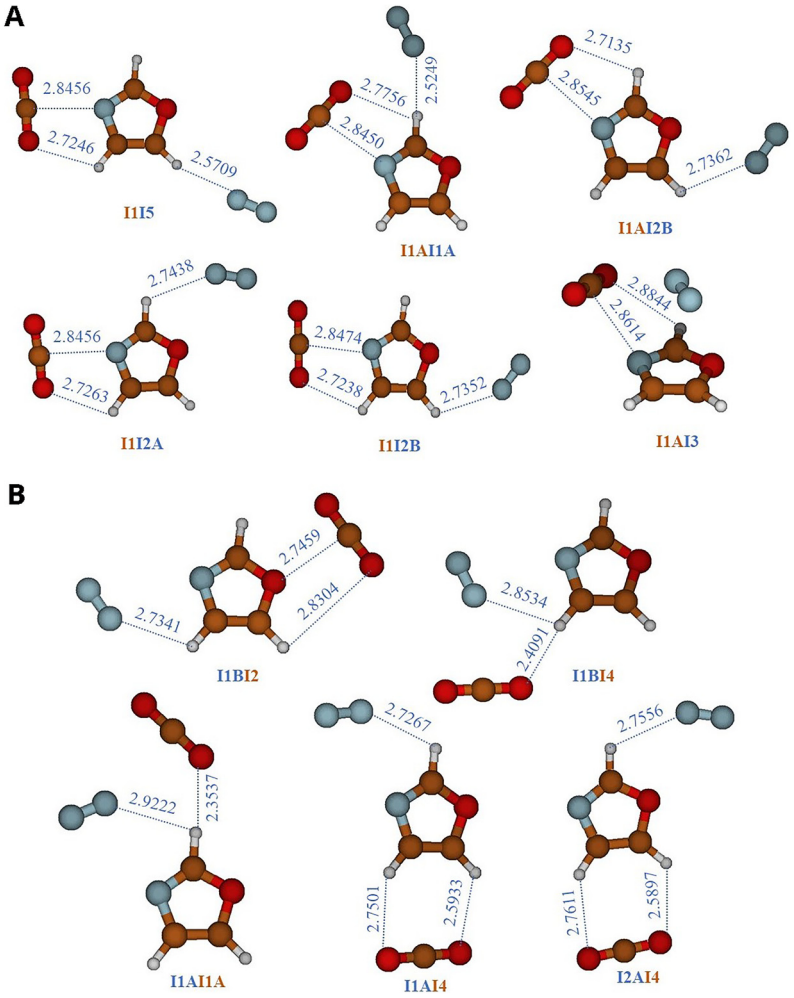

Figure 3. Three-body complexes composed by CO_2-Oxa-N_2. A) CO_2-Oxa + N_2 complexes, they are labeled using the symbol "InIm"."n" denotes the location of CO_2 and "m" refers to the position of N_2. **B**) N_2-Oxa + CO_2 complexes, they are labeled using the symbol "ImIn"." m " denotes the location of N_2 and "n" refers to the position of CO_2.

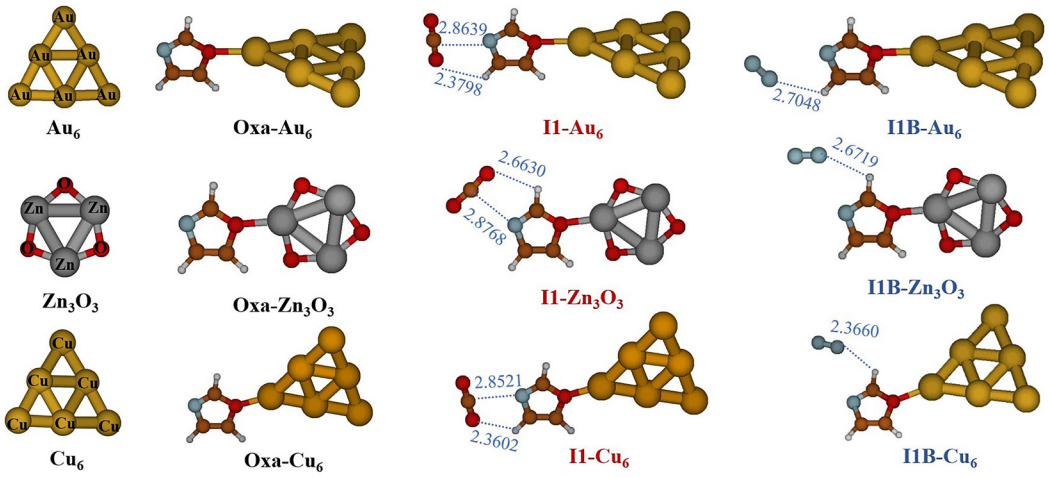

Figure 4. Optimized structures of Oxa-Au_6, Cu_6 and Zn_3O_3 and of CO_2/N_2-Oxa- Au_6, Cu_6 and Zn_3O_3 complexes at MP2/AVDZ/LanL2DZ level of theory.

O10 and H6 of the Oxazole breaks, and a new hydrogen bond forms between O11 and H7 of the Oxazole. The calculated MP2/AVDZ/ LanL2DZ Binding energies (BEs) of the CO_2/N_2–Oxa-Au_6, Cu_6 and Zn_3O_3 complexes are listed in Table 7. Our results show that metallic and metal oxide clusters favor the adsorption of CO_2 and N_2 gases. In hexametallic clusters, the adsorption energies (E_b) reach a maximum with the Cu_6 cluster, at -6.46 kcal/mol for CO_2 and -10.25 kcal/mol for N_2. However, the Au_6 and Zn_3O_3 clusters exhibit similar binding energy values: E_b(Au_6-I1) = -4.58 kcal/mol and E_b(Zn_3O_3-I1) = -4.56 kcal/mol for CO_2, and E_b(Au_6-I1) = -2.19 kcal/mol and E_b(Zn_3O_3-I1) = -2.22 kcal/mol for N_2. This is highly advantageous as it allows for the replacement of expensive gold clusters with more cost-effective materials such as Zn_3O_3.

Adsorption of CO_2 and N_2 in the metal and metal oxide surfaces (111)

The molecular simulation (Monte Carlo) was conducted to examine the adsorption of CO_2 and N_2 on Au, Cu, and ZnO (111) surfaces. The choice of Au (111) and Cu (111) surfaces is motivated by the interest in the interaction of small molecules Au (111) surface. Furthermore, adsorption on noble metals (such as Cu, Ag, and Au) is considered a promising avenue for materials in future technologies and applications[67], however, the selection of ZnO aims to ensure high efficiency in the low-cost adsorption of pollutants. The investigation commenced with optimizing the geometries of the Oxa-CO_2 and Oxa-N_2 complexes using the COMPASS II force field in the Forcite Module. Subsequently, we constructed three-layer models for each surface (Au(111), Cu(111), and ZnO(111)). In the Adsorption Locator Module, we selected one of these surfaces and added the adsorbate, either Oxa-CO_2 or Oxa-N_2, before running the calculations. This process was repeated for all surfaces. The optimized geometries and their corresponding adsorption energies are depicted in the Figure 5. The calculations show spontaneous physisorption of CO_2 and N_2. Additionally, the ZnO surface is the most favorable for N_2 adsorption compared to CO_2, with an adsorption energy of -151.62 kcal/mol for N_2, while for CO_2, it reaches -148.01 kcal/mol. However, for the two other surfaces, Cu (111) and Au (111), the adsorption of CO_2 is more favorable than that of N_2, with respective adsorption energy values of -36.97 kcal/mol and -32.88 kcal/mol for Au, and -22.27 kcal/mol and -19.52 kcal/mol for Cu (111). Overall, our calculations demonstrate that the surfaces of gold (Au), copper (Cu), and zinc oxide (ZnO) are capable of adsorbing N_2 and CO_2 from gas mixtures. Moreover, ZnO and Cu offer advantages in terms of adsorption capacity for both gases, without introducing additional cost-related issues.

Table 7. MP2/AVDZ/LanL2DZ binding energies of the CO_2/N_2–Oxa-Au_6, Cu_6 and Zn_3O_3 complexes (E_b, kcal/mol).

		Au_6	Cu_6	Zn_3O_3
Complexes	**I1**	**I1**	**I1**	**I1**
Oxa-CO_2	-4.48	-4.58	-6.46	-4.56
Oxa-N_2	-1.77	-2.19	-10,25	-2.22

Sorption isotherms

The adsorption isotherms of Oxa-CO_2 and Oxa-N_2 on Au (111), Cu (111), and ZnO (111) surfaces were calculated with the GCMC[68,69] procedure implemented in the sorption module in BIOVIA Materials Studio. These simulations were carried out in the μVT ensemble, where the chemical potential (μ), volume (V), and temperature (T) are held constant, allowing the number of gas molecules in the system to fluctuate naturally in response to the external reservoir. All simulations were performed at 298 K over a pressure range of 1000 to 10,000 kPa. The chemical potential corresponding to each pressure point was determined using the Peng–Robinson equation of state, which accounts for non-ideal gas behavior. The Metropolis algorithm was applied to sample system configurations through stochastic insertion, deletion, translation, and rotation of molecules, ensuring ensemble consistency. Long-range electrostatic interactions between the adsorbates and the surfaces were calculated using the Ewald summation method with an energy accuracy of 0.001 kcal/mol, while van der Waals interactions were modeled using the atom-based method with a cutoff distance of 12.5 Å. Each simulation consisted of 10,000 loading steps for system equilibration and 100,000 production steps to collect statistically meaningful adsorption data. This computational approach provides detailed insight into the pressure-dependent adsorption behavior of Oxazole-functionalized gases on metallic

The GCMC adsorption isotherm is a key tool for evaluating and quantifying the gas adsorption capacity on the hosts. The adsorption isotherms of Oxa-CO_2 and Oxa-N_2 on Au (111), Cu (111), and ZnO (111) surfaces, presented in Figure 6, reveal that all three surfaces generally exhibit better adsorption performance for CO_2 compared to N_2.

For instance, at a pressure of 19 bars, the average loading of Oxa-CO_2 is 57 molecules per unit cell on ZnO (111), and 69 molecules per unit cell on both Cu (111) and Au (111), whereas for Oxa-N_2, the values are 56.6 molecules per unit cell for ZnO (111), 68.8 molecules per unit cell for Cu (111), and 65.9 molecules per unit cell for Au (111). When the pressure increases to 91 bars, the number of CO_2 molecules adsorbed reaches 65 molecules per unit cell on ZnO (111), and 79 molecules per unit cell on both Cu (111) and Au (111), while for Oxa-N_2, the values reach 61, 74.5, and 76 molecules per unit cell, respectively.

In the case of Oxa-CO_2, the ZnO (111) surface appears to reach saturation adsorption equilibrium at a relatively high pressure, around 73 bars. In contrast, for Oxa-N_2, equilibrium seems to be reached earlier, around 46 bars.

Given the trend of the adsorption isotherms, it is likely that the Au (111) and Cu (111) surfaces only reach adsorption equilibrium at around 55 bars for gold and 73 bars for copper in the case of Oxa-CO_2. On the other hand, for Oxa-N_2, adsorption continues to increase significantly with

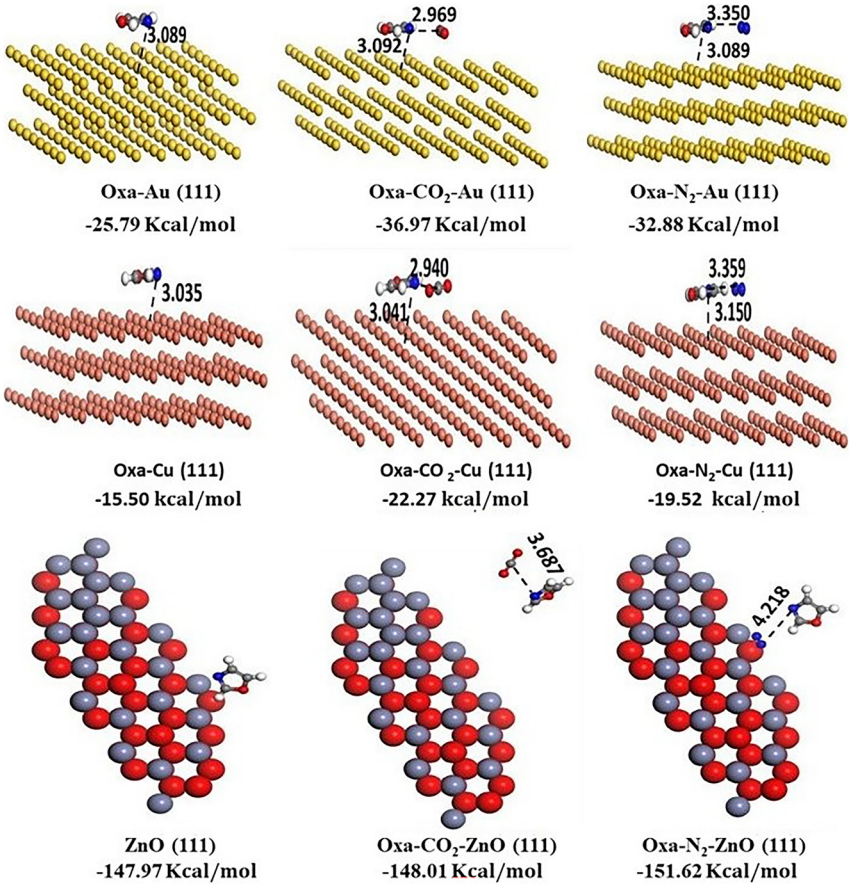

Figure 5. **Optimized structures of Oxa- Au (111) /Cu (111) and ZnO (111) and of CO_2/N_2–Oxa@ Au (111)/ Cu (111) and ZnO (111) complexes, derived from the MC simulation.**

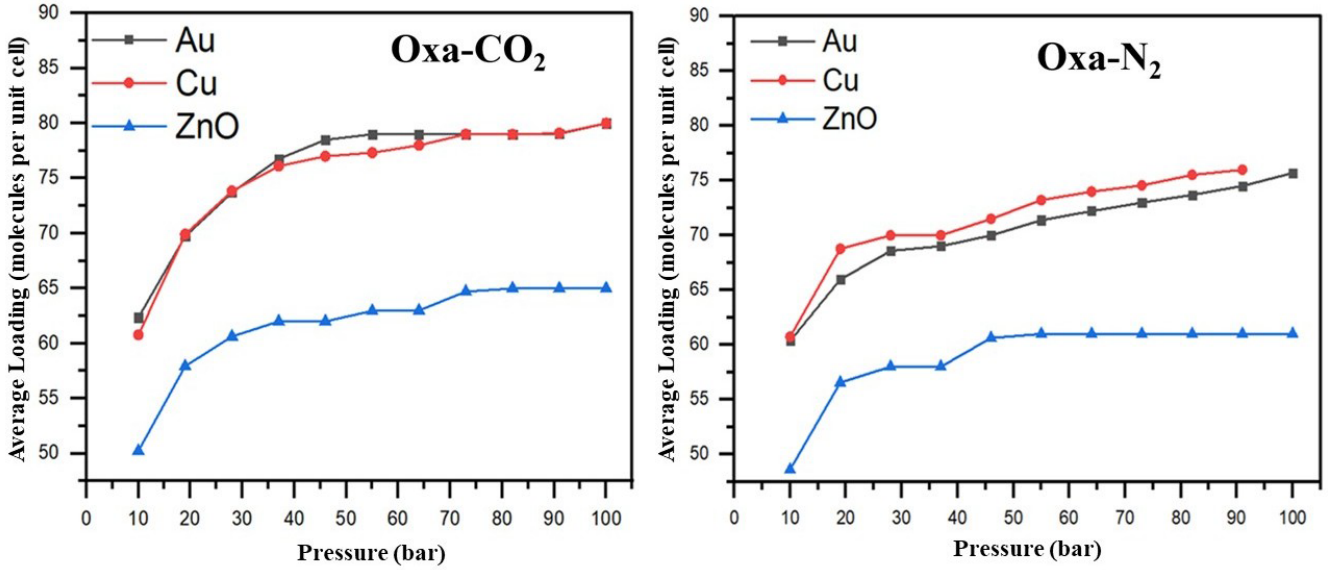

Figure 6. **Calculated Oxa-CO_2 and Oxa-N_2 adsorption isotherms at 298 K on Au (111), Cu (111), and ZnO (111) surfaces.**

rising pressure. Therefore, the Cu surface, in particular, is expected to offer even greater adsorption capacity for both CO_2 and N_2 at higher pressures.

Conclusion

In summary, Our study demonstrates that Oxazole has a significant adsorption capacity for both CO_2 and N_2, with a notably higher capacity for CO_2. The presence of a second gas does not affect Oxazole's ability to capture both gases simultaneously, but it may enhance adsorption through the formation of hydrogen bonds among the three systems. The addition of clusters Au_6, Cu_6, and Zn_3O_3 to the most stable structures I1 of the Oxa-CO_2 complex and I1A of the Oxa-N_2 complex increases the adsorption capacity for both gases, with Cu_6 exhibiting the highest capacity compared to Au_6 and Zn_3O_3. Finally, the investigation of interactions between the most stable structures of the Oxa-CO_2 and Oxa-N_2 complexes with the three (111) surfaces of Au, Cu, and ZnO demonstrates that gold (Au), copper (Cu), and zinc oxide (ZnO) surfaces are capable of adsorbing N_2 and CO_2 from gas mixtures. Moreover, Cu offer advantages in terms of adsorption capacity for both gases, without introducing additional cost-related issues.

Ethics and consent

Ethics and consent were not required.

Data availability statement

No data are associated with this article

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Version 4

Reviewer Report 26 September 2025

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✔ **Driss benabdallah**
[1] University of Tunis El Manar, Tunis, Tunis, Tunisia
[2] University of Carthage Preparatory Institute for Engineering Studies of Nabeul (Ringgold ID: 198832), Mrezga, Nabeul, Tunisia

It's OKay

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: My area of expertise is in non-reactive molecular dynamics, particularly ab initio calculations of potential energy surfaces for van der Waals systems, followed by the calculation of rotational transition cross-sections from molecular collisions, and the subsequent determination of collisional rate coefficients.

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard.

Version 3

Reviewer Report 17 September 2025

https://doi.org/10.21956/openreseurope.23131.r60087

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✔ **Driss benabdallah**

[1] University of Tunis El Manar, Tunis, Tunis, Tunisia
[2] University of Carthage Preparatory Institute for Engineering Studies of Nabeul (Ringgold ID: 198832), Mrezga, Nabeul, Tunisia

The authors have carefully addressed the comments raised in the previous review. The revised manuscript shows clear improvements in clarity, consistency, and scientific accuracy.
Notably, the consistent use of notation ("CO_2–Oxa" and "N_2–Oxa"), the inclusion of additional computational details (CCSD(T)-F12b validations), and the updated figures and tables have strengthened the overall quality of the paper. The rephrasing of sentences has also improved readability.
I consider that the authors have satisfactorily resolved the concerns raised in my earlier report.

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: My area of expertise is in non-reactive molecular dynamics, particularly ab initio calculations of potential energy surfaces for van der Waals systems, followed by the calculation of rotational transition cross-sections from molecular collisions, and the subsequent determination of collisional rate coefficients.

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard.

Version 2

Reviewer Report 10 September 2025

https://doi.org/10.21956/openreseurope.21961.r58175

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Dharamashi Rabari
Ahmedabad University, Ahmedabad, Gujarat, India

The research article explores molecular interactions through ab initio calculations. The findings suggest strong selectivity for CO2 over N2.

It can be accepted with following minor revisions.

- Oxazole is first introduced without abbreviation; later, you use "Oxa." Please introduce the abbreviation at first mention, e.g., *"oxazole (Oxa)" in introduction itself*
- The statement *"I recommend the open-source software Quantum ESPRESSO and CP2K"* can be rephrased to a neutral tone
- Maintain uniform usage: e.g., *"Oxazole–N_2"* instead of switching between *"Oxazole-N_2"*

and *"oxazole-N2."*Similarly, use consistent formatting for *Oxazole–CO_2*.
- In Figure 1, the atom is marked as "H6," while in the text it is referred to as *"Hydrogen 6."* Please check.
- Figure 6: Specify the adsorption loading units used
- Revise "In summary,Our study" to "In summary, Our study" (spacing).
-
    - Oxazole is first introduced without abbreviation; later, you use "Oxa." Please introduce the abbreviation at first mention, e.g., *"oxazole (Oxa)" in introduction itself*
    - The statement *"I recommend the open-source software Quantum ESPRESSO and CP2K"* can be rephrased to a neutral tone
    - Maintain uniform usage: e.g., *"Oxazole–N_2"* instead of switching between *"Oxazole-N_2"* and *"oxazole-N2."*Similarly, use consistent formatting for *Oxazole–CO_2*.
    - In Figure 1, the atom is marked as "H6," while in the text it is referred to as *"Hydrogen 6."* Please check.
    - Figure 6: Specify the adsorption loading units used
    - Revise "In summary,Our study" to "In summary, Our study" (spacing).

Is the work clearly and accurately presented and does it cite the current literature?
Yes

Is the study design appropriate and does the work have academic merit?
Yes

Are sufficient details of methods and analysis provided to allow replication by others?
Yes

If applicable, is the statistical analysis and its interpretation appropriate?
Yes

Are all the source data underlying the results available to ensure full reproducibility?
Yes

Are the conclusions drawn adequately supported by the results?
Yes

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: Computational chemistry, Molecular Simulation, Deep Eutectic Solvents Applications

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard.

Reviewer Report 28 August 2025

https://doi.org/10.21956/openreseurope.21961.r57379

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Driss benabdallah
[1] University of Tunis El Manar, Tunis, Tunis, Tunisia
[2] University of Carthage Preparatory Institute for Engineering Studies of Nabeul (Ringgold ID: 198832), Mrezga, Nabeul, Tunisia

The manuscript is well written and easy to follow, with a clear structure and a good selection of recent references. The study uses a combination of *ab initio* MP2 calculations and Monte Carlo simulations for two-body, three-body, and surface adsorption systems. This approach is well suited to the topic and gives results of clear scientific interest, especially showing that oxazole binds more strongly to CO_2. The methods are described in enough detail to allow other researchers to repeat the work, although providing input files, Cartesian coordinates, and raw energies would make reproduction easier. No formal statistical analysis is needed, and the way the results are interpreted is reasonable. However, since there are no datasets linked to the article, sharing the source data would make the work more transparent and repeatable. The conclusions are supported by the structural, energetic, and adsorption isotherm results, and the suggested minor revisions are mainly to improve clarity, consistency, and small methodological points.

Main Points for Revision
1. Clarity and presentation
   - Repetition error – Page 4, line ~16:
     Replace 'to estimate the adsorption isotherms to estimate the adsorption isotherms' with:
     "...performed to estimate the adsorption isotherms of oxazole@CO_2 and oxazole@N_2 on Au(111), Cu(111), and ZnO(111) surfaces."
   - Grammar – Page 4, line ~27:
     "I recommend the open-source software Quantum ESPRESSO and CP2K" → replace 'software' by 'software packages'.
   - Clarity – Page 5, lines 1–3:
     Rewrite awkward sentence on structure optimization:
     "The structures of oxazole, oxazole@N_2, and oxazole@CO_2 were optimized to obtain their lowest-energy configurations using the COMPASS II force field, as implemented in the Forcite Module."
   - Paragraph restructuring – Page 6, lines 3–8:
     Rewrite for clarity:
     "This section examines the adsorption and activation of CO_2 and N_2 on small metal clusters (Au_6, Cu_6) and on the metal oxide cluster Zn_3O_3. Even-numbered clusters were chosen because they tend to be more stable and have larger HOMO–LUMO gaps, ensuring reliable structures during adsorption studies."
   - Proofreading – Final check for grammar and typographic consistency.
2. Methodological details
   - Computational details – Page 5, line ~20:
     Clarify basis sets for metals and non-metals:

"...MP2 method with aug-cc-pVDZ for non-metals and LANL2DZ ECP for metals."
- Validation of MP2 – Suggest running a single-point CCSD(T)-F12 calculation on one representative complex (CO_2–Oxa or N_2–Oxa) to confirm MP2 accuracy.

3. Consistency and formatting
   - Notation consistency – Throughout manuscript:
     Use "CO_2–Oxa" instead of "Oxa@CO_2" for clarity and ensure consistent A/B labeling (CO_2 = A, N_2 = B).
   - Figure/Table consistency –
     - Table 1: bold CO_2 as for Oxazole.
     - Table 3: bold N_2, check "ER" vs "Er".
     - Table 5: fix "Oxazole-0N_2" → "Oxazole–N_2".
     - Figures 2A/2B: clarify I1A, I2B, etc.

Is the work clearly and accurately presented and does it cite the current literature?
Yes

Is the study design appropriate and does the work have academic merit?
Yes

Are sufficient details of methods and analysis provided to allow replication by others?
Yes

If applicable, is the statistical analysis and its interpretation appropriate?
Not applicable

Are all the source data underlying the results available to ensure full reproducibility?
No

Are the conclusions drawn adequately supported by the results?
Yes

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: My area of expertise is in non-reactive molecular dynamics, particularly ab initio calculations of potential energy surfaces for van der Waals systems, followed by the calculation of rotational transition cross-sections from molecular collisions, and the subsequent determination of collisional rate coefficients.

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.

Reviewer Report 27 August 2025

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Nguyen Thi Xuan Huynh
Quy Nhon University, Quy Nhon City, Vietnam

There are no comments for the revised version.

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: Computational physics, Computational Physical Chemistry

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard.

Version 1

Reviewer Report 18 March 2025

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Nguyen Thi Xuan Huynh
Quy Nhon University, Quy Nhon City, Vietnam

I have some additional suggestions as follows:
1. Check for spelling errors and wordiness in some places, and make sure it is concise and meaningful. For example, whether or not there is a comma "," or whether "the Figure ..." is used before the Figure, plural or singular, etc. There are many spelling mistakes in the manuscript, such MOF's (MOFs), labelling (labeling),...
2. Consistent use of kcal/mol energy units for Er (relative energies) in Tables 1 and 2, consistent with the data used in the text. Unify the use of the units in kcal/mol or kcal.mol^-1...
3. Calculations should be focused in the "Calculation details" section without needing to be explained separately in the results and discussion sections.
4. The authors should only give important information in the Conclusion section. For example, the authors can omit the first sentence about the method.
5. Please describe the Monte Carlo simulation method in more detail. This simulation method can quantify the gas adsorption capacity on the hosts. The authors should supplement their calculation results through adsorption isotherms.
6. The authors need to further elucidate the interactive nature of important adsorption systems through density of states or charge density differences.

7. Replace the figures due to blur and have to underline the captions, as shown in Figure 5.
8. Check your references in manuscript. Note that the superscript numerals are placed after quotation marks, commas, and periods.

Is the work clearly and accurately presented and does it cite the current literature?
Partly

Is the study design appropriate and does the work have academic merit?
Yes

Are sufficient details of methods and analysis provided to allow replication by others?
Yes

If applicable, is the statistical analysis and its interpretation appropriate?
Yes

Are all the source data underlying the results available to ensure full reproducibility?
Yes

Are the conclusions drawn adequately supported by the results?
Partly

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: Computational physics, Computational Physical Chemistry

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.

Author Response 25 Apr 2025

samira dalbouha

We sincerely thank the reviewer for their valuable comments on our manuscript. These constructive remarks and suggestions have significantly contributed to the improvement of our work. In response to these comments, we have prepared a revised and enhanced version of the manuscript. *(The reviewer's comments are presented in italics.)* ***Comment-1 :*** *Check for spelling errors and wordiness in some places, and make sure it is concise and meaningful. For example, whether or not there is a comma "," or whether "the Figure …" is used before the Figure, plural or singular, etc. There are many spelling mistakes in the manuscript, such MOF's (MOFs), labelling (labeling),…* ***Reply-1 :*** We have carefully reviewed the manuscript and addressed the spelling errors and wordiness issues as suggested. Proper punctuation has been ensured, singular/plural usage corrected, and references to figures standardized. Additionally, the specific spelling mistakes mentioned, such as *MOF's* (corrected to *MOFs*) and *labelling* (corrected to *labeling*), have been revised accordingly. ***Comment-2 :*** *Consistent use of kcal/mol energy units for Er (relative energies) in Tables 1 and 2, consistent with the data*

used in the text. Unify the use of the units in kcal/mol or kcal.mol^-1... ***Reply-2 :*** We have taken your suggestion into account and have unified the use of energy units in Tables 1 and 2. The relative energy values (Er) are now consistently expressed in kcal/mol, in line with the data used in the text. ***Comment-3 :*** *Calculations should be focused in the "Calculation details" section without needing to be explained separately in the results and discussion sections.* ***Reply-3 :*** We have taken your suggestion into account and moved the calculation details to the "Calculation Details" section. ***Comment-4 :*** *The authors should only give important information in the Conclusion section. For example, the authors can omit the first sentence about the method.* ***Reply-4 :*** We have revised the Conclusion section to include only the essential information, omitting the first sentence regarding the method, as suggested, to make it more concise and focused on the key results. ***Comment-5 :*** *Please describe the Monte Carlo simulation method in more detail. This simulation method can quantify the gas adsorption capacity on the hosts. The authors should supplement their calculation results through adsorption isotherms.* ***Rpply-5 :*** We have taken your suggestion into account and added a detailed description of the Monte Carlo simulation method in the article. Additionally, a new section titled "sorption Isotherms" has been included, along with Figure 6, which illustrates the adsorption isotherms. These additions complement our calculation results and allow for the quantification of the gas adsorption capacity on the hosts. ***Comment-6 :*** *The authors need to further elucidate the interactive nature of important adsorption systems through density of states or charge density differences.* ***Reply-6 :*** We thank the reviewer for this insightful comment. We would like to clarify that this article is part of a series of studies conducted within the framework of our research project on the adsorption of pollutant gases. A detailed investigation of the interactive nature of the adsorption systems, particularly through density of states (DOS) and charge density difference analyses, will be presented in a complementary article currently in preparation, which will specifically focus on the electronic aspects of the systems studied here. ***Comment-7 :*** *Replace the figures due to blur and have to underline the captions, as shown in Figure 5.* ***Reply-7:*** We have taken your comment into account. All the blurred figures have been replaced with higher-quality versions, specifically Figures 1, 2, 3A, 3B, and 5. ***Comment-8 :*** *Check your references in manuscript. Note that the superscript numerals are placed after quotation marks, commas, and periods.* ***Reply-8 :*** We have taken your comment into account and revised the manuscript accordingly. The superscript reference numerals have been repositioned to appear after quotation marks, commas, and periods, as required.

Competing Interests: No competing interests were disclosed.

Comments on this article

Version 2

Reviewer Response 05 Aug 2025

Xuan Huynh Nguyen

There are no comments for this version. I agree with the revised version.

Competing Interests: No competing interests were disclosed.