Computational Modelling of Adsorption and Diffusion Properties of CO_2 and CH_4 in ZIF-8 for Gas Separation Applications: A Density Functional Theory Approach

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Supplementary Information

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1. Material Structure

The structure of ZIF-8 has atoms arranged in a sodalite topology with Zn^{2+} ions tetrahedrally coordinated by methylimidazolate (mim) linkers. ZIF-8 has a cubic crystal structure with a space group of $I-\bar{4}3m$ (number 217) and a framework formula of $Zn(mim)_2$.[1] The conventional cell is depicted in Figure S1a and is adopted for the calculations reported in this work. The sodalite topology contains large pores (cages) with a diameter of 11.6 Å. The large pore appears at the center of the conventional cell in Figure S1b and is marked with a yellow sphere.

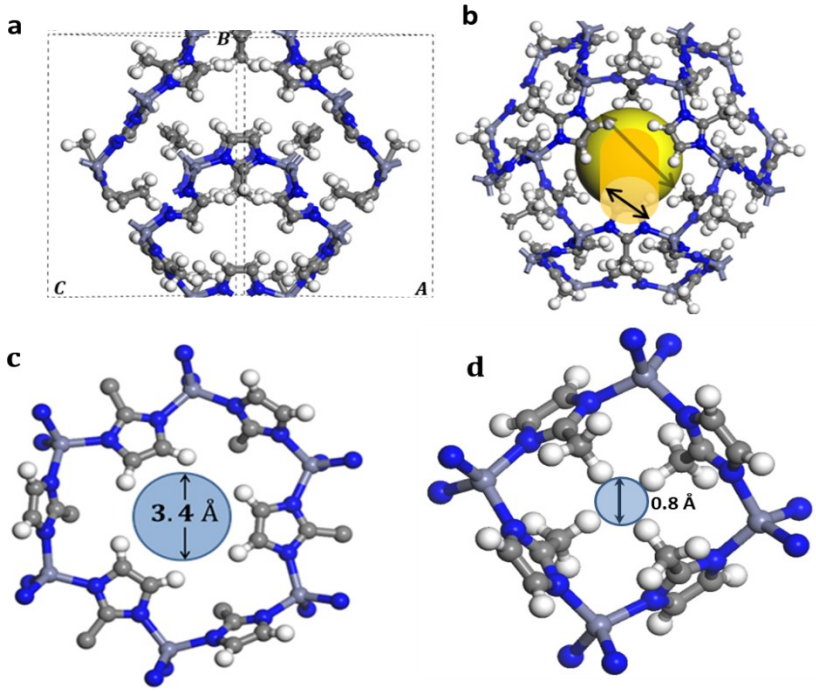

Figure S1: Schematic of a conventional unit cell (a). The central pore (cage) of diameter 11.6 Å is shown with a yellow sphere, and 6-membered ring of diameter 3.4 Å is shown with an orange channel (b). The 6-MR (c) and 4-MR (d) are depicted with diameters of 3.4 Å and 0.8 Å, respectively. The color codes for C, N, Zn and H are dark grey, blue, light grey and white, respectively.

Surrounding the central pore are eight apertures or windows made of 6-membered rings (6-MR), each with C_{3v} symmetry and with a diameter of approximately 3.4 Å. While three of the methylimidazolate linkers lie almost in the plane of the window, three are tilted with respect to the plane of the window. Due to the tilting of the linkers, the areas on either side of the 6-membered rings are not symmetrically equivalent. In Figure S1c, a 6-membered ring is shown along the [111] direction. Also surrounding the central pore are six smaller windows made of 4-membered rings (4-MR) with D_{2d} symmetry and diameters of approximately 0.8 Å, lying on the six faces of the conventional cell. A 4-membered ring is shown in Figure S1 d along the [100] direction.

The central cage and the windows through which guest molecules can diffuse are depicted in Figure S1 b. The windows with diameter of 3.4 Å were found to allow diffusion of molecules larger than its diameter through a process widely believed to be a "window breathing".[2]

2. Structural and Electronic properties

The DFT-optimized values of lattice parameters for ZIF-8 are $a = 17.036$ Å, $b = 17.035$ Å, $c = 17.037$ Å. These values are in excellent agreement with the experimentally measured values of $a = b = c = 16.99$ Å.[1] The equilibrium volume of the unit cell is found to be 4958.821 $Å^3$ which is comparable to the experimentally measured volume of 4905.2 $Å^3$.[1] The angles α, β and γ are all calculated to be within 1% of the experimentally measured value of $\alpha = \beta = \gamma = 90°$. The distances between two Zn atoms, as indicated in Figure S2**a**, are found to be in the range of 6.018 to 6.037 Å, which compares very well with the experimental result of 6.007 Å.

There are four key structural features evident from the experimental structure that are reproduced well by the DFT optimization (Figure S2 a, b). The first involves the three imidazolate linkers that protrude into window created by the 6-MR. The distance between carbon atoms from adjacent linker molecules is calculated to be 5.011 Å. This is comparable with the experimental value of 5.085 Å. The second key structural feature noted is the distance between the two C atoms of the methyl groups on opposite sides of 4-MR. This C-C distance is calculated to be 4.505 Å, in good agreement with the experimental value of 4.513 Å. Third, as previously mentioned, three of the imidazolate linkers are nearly planar with respect to the plane of the window formed by the 6-

MR, while the other three are tilted by the angle δ with respect to the plane of the window. The angle δ is calculated to be 113.4°, which compares remarkably well to the experimental value of 114.8° as shown in Figure S2 **a**. Finally, the calculated value for each of the angles α, β and γ is 89.95° which agrees well with the experimental value for cubic geometry. We summarize the lattice parameters and electronic properties in Table S1.

Table S1 Lattice parameters, bond lengths and bond angles in ZIF-8

Crystal structure	Cubic (Sodalite topology)
Space group	$I\bar{4}3m$
Framework formula	$Zn(mim)_2$
Unit structure	$C_8H_{10}N_4Zn$
Lattice parameters (Å)	Calculated (Experiment[21])
a	17.036(16.999)
b	17.035(16.999)
c	17.037 (16.999)
Angle (°)	$\alpha = \beta = \gamma = 89.95$ (90)
Volume (**Å³**)	4958.821(4905.20)
Central pore volume (**Å³**)	2500
6-MR diameter (**Å**)	3.4
4-MR diameter (**Å**)	0.8
Bond lengths (Å) and bond angles (°)	
$d_{C\text{-}C}$ (6-MR)	5.011 (5.085)
$d_{C\text{-}C}$ (Methyl group in 4-MR)	4.505 (4.513)
$d_{Zn\text{-}Zn}$	6.018 – 6.037 (6.007)
δ	113.4° (114.8°)
θ	62.15° (62.10°)
Bang gap (eV)	4.38 (5.1[54])

As a part of the electronic structure calculation, we also performed a total density of states (DOS) calculation with and without the van der Waals interaction. The DOS reveals the probability of states as a function of energy and allows us to assess the band gap. The predicted band gap is found to be 4.38 eV (100.78 kcal/mol) which is about 85 % of the experimental value.[3, 4]

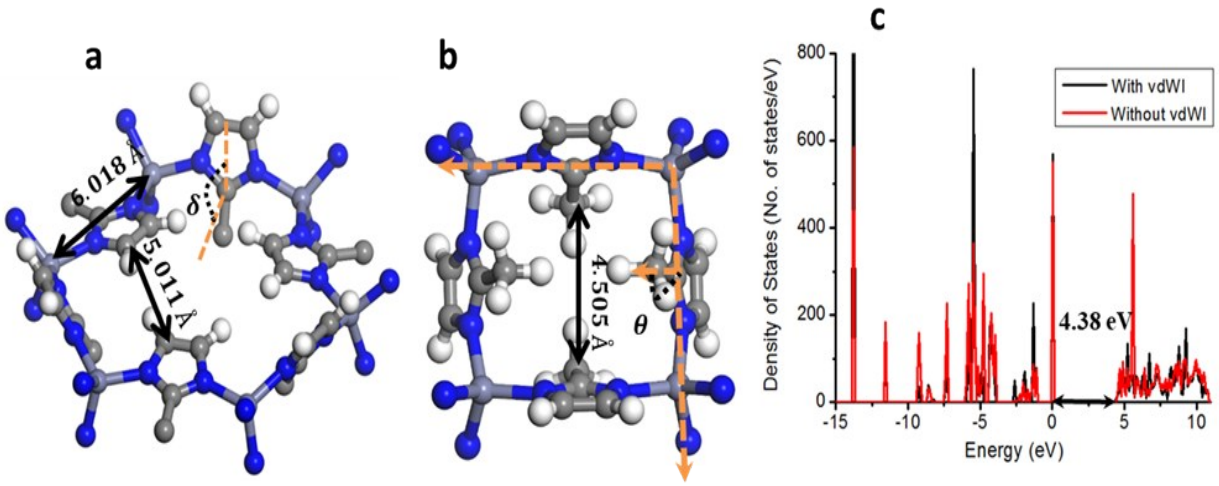

Figure S2: Key structural parameters in 6-MR (**a**) and 4-MR (**b**). The value of angles δ and θ are 113.4° and 62.15°, respectively. Density of states (DOS) of bulk ZIF-8 calculated with (black) and without (red) van der Waals interaction (vdWI) (**c**).

3. Gas adsorption sites

Our calculations show that the most stable binding site for CO_2 is located 3.81 Å right below one of the C atoms of imidazolate ring as shown in Figure S3 **a**. The alignment of the molecule is in a plane parallel to the nearest ring with an adsorption energy of -5.01 kcal/mol. The absolute value of the adsorption energy can be compared with the experimentally observed value of the isosteric heat of adsorption which is 4.67 kcal/mol.[5] The reported experimental value is for zero coverage limit. At low coverage limit, the interaction between framework and the molecule is strong. As the coverage limit is increased, molecules start interacting each other in addition to their interaction to the framework. This reduces the isosteric heat absorption at higher coverage limit. Gadipelli *et al*[6] reported the heat of adsorption to be 4.01 kcal/mol in ZIF-8, whereas the heat of adsorption for a sample that is thermally annealed just below the framework decomposition temperature is 7.1 kcal/mol at 1 bar and 25 °C. We do not have temperature effect in DFT calculated results, and therefore our results neglect any contribution arising from the entropy changes at higher temperature than 0 K. The second-most stable binding site for CO_2 is found to lie near the pore with an adsorption energy of 4.89 kcal/mol. Figure S3 **b** shows energy landscape of different sites we studied here. Near

the center of the cage, the adsorption energy decreases to -1.86 kcal/mol as the gas molecule at this site weakly interacts with the framework. The sites IV and V have energy difference of about 0.12 kcal/mol to each other. The uncertainty in the energy per Å applied on each atom in our calculation is 0.01 (eV/ Å), which is decided by one of the precision controlling parameters of VASP, the cutoff energy. In this view, above energy difference is within the error bar of 0.25 kcal/mol of our calculation method.

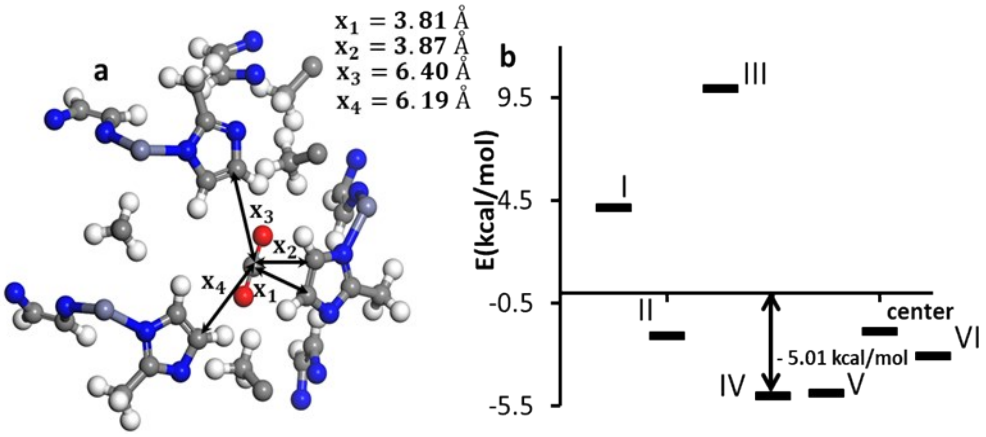

Figure S3: The site with strongest adsorption energy for a CO_2 molecule (**a**). The position of CO_2 molecule in reference to the framework's atoms are also presented. Few different adsorption sites for CO_2 (**b**). The 'center' represents the binding of CO_2 near the center of the cage.

In the Figure S4, we present most stable site with highest adsorption energy for CH_4 in the framework. We find that the most stable site lies about 4 Å from one of the imidazolate linkers that form the 6-MR. CH_4 binds at this site with an adsorption energy of -4.50 kcal/mol. In ref.[7] the experimental heat of adsorption at low loading limit for CH_4 (for initial molecule of CH_4) has been reported to be 2.87 kcal/mole (note the sign convention between our calculated adsorption energy and reported heat of adsorption) . This was obtained by extrapolation of isotherm data to the low-pressure regime which presents the uncertainty in the result. Hence, it still lacks a proper experimental measurement of heat of adsorption which we can compare with the DFT calculated result. It is noted that both, our calculation, and the experimental data, suggest that CO_2 has a

higher heat of adsorption than CH_4, indicating that CO_2 interaction with ZIF-8 is stronger than CH_4-ZIF-8 interaction.

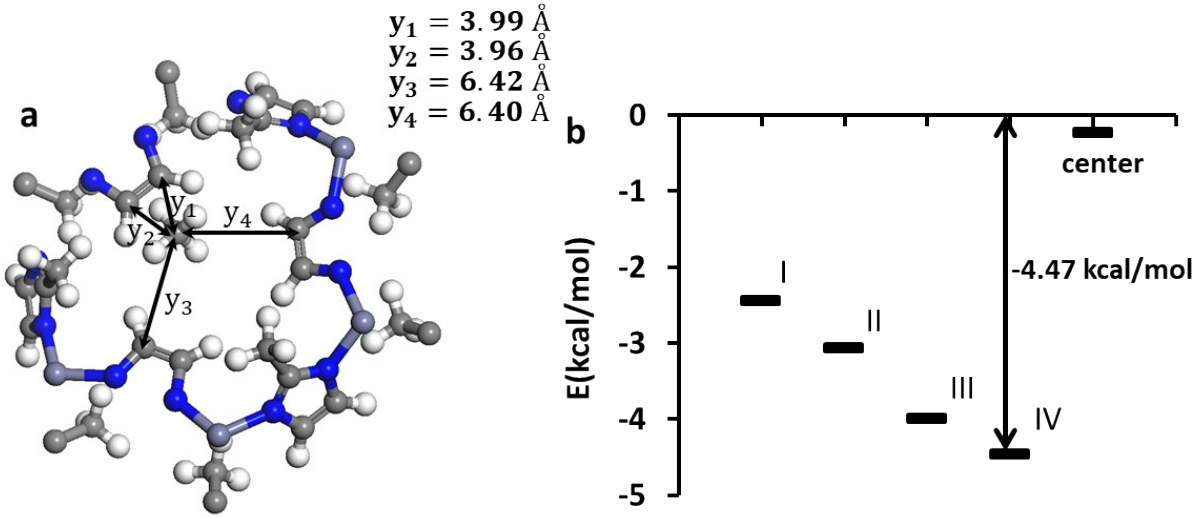

Figure S4: The site with strongest adsorption energy for a CH_4 molecule (**a**). The position of CH_4 molecule in reference to the framework's atoms are also presented. Four different adsorption sites for CO_2 (**b**). The 'center' represents the binding of CH_4 near the center of the cage.

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