H₂, N₂ and CH₄ Gas Adsorption in Zeolitic Imidazolate Framework-95 and -100: *Ab Initio* based Grand Canonical Monte Carlo Simulations

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Abstract

A multiscale approach based on *ab initio* and grand canonical Monte Carlo (GCMC) simulations is used to report the H₂, N₂, and CH₄ uptake behaviors of two Zeolitic Imidazolate Frameworks (ZIFs), ZIF-95 and -100, with exceptionally large and complex colossal cages. The force fields describing the weak interactions between the gas molecules and ZIFs in GCMC simulations are based on *ab initio* MP2 level of theory aimed at accurately describing the London dispersions. We report the total and excess gas uptakes up to 100 bar at 77 and 300 K. Our results unravel the interplay between the uptake amount, pore volume, guest molecule size, temperature, chlorine functional group and isosteric heat of adsorption in ZIFs. We found that while the uptake capacity of ZIF-100 outperforms ZIF-95 for small molecules (H₂), ZIF-95 offers a superior adsorption capacity for large molecules (CH₄). Moderately sized molecules (N₂) exhibit a more complex uptake behavior depending on the temperature. Furthermore, we show that the induced dipole interactions, such as those caused by –Cl functional groups, play a vital role on gas adsorption behaviors. This work provides the first report on the N₂ and CH₄ uptake of ZIF-95 and -100 using *ab initio* based GCMC simulations.

**Keywords:** Uptake Capacity, *Ab Initio* GCMC simulations, Functional Group, ZIF-95, ZIF-100

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1. Introduction

A holistic understanding of the gas adsorption processes is of paramount importance for developing efficient storage nanoporous materials. Zeolitic imidazolate frameworks (ZIFs) are a new subclass of porous metal organic frameworks (MOFs) emerging as new alternative nanoporous materials for gas storage and gas separation applications.\textsuperscript{1,2,3} ZIFs have tetrahedral networks that resemble those of zeolites with transition metals (Zn(II), Co(II), etc.,) linked by imidazolate ligands.\textsuperscript{2,4} The great features of these materials for application in gas storage and separation processes is mainly due to their exceptional chemical and thermal stabilities.\textsuperscript{2} Numerous investigations have been performed to study gas adsorption isotherms as well as separation of gas mixture, which is important in industrial gas purification processes.\textsuperscript{5,6,7,8,9,10,11,12} Yaghi and co-workers synthesized and characterized several new types of porous ZIFs based materials, containing Zn(II) and Co(II) metal connecters and imidazolate (Im) and benzimidazolate (BI) linkers with chlorine (–Cl) substituent in the aromatic ring.\textsuperscript{3} Wu et al. have investigated H\textsubscript{2} adsorption sites and binding energies in ZIF-8 using a combined experimental and computational method.\textsuperscript{6} Yildirim\textsuperscript{6,7} group measured the adsorption of H\textsubscript{2} and CH\textsubscript{4} on ZIF-8 over large temperature and pressure ranges. Pellitero et al.\textsuperscript{13} examined adsorption of CO\textsubscript{2}, CH\textsubscript{4}, and N\textsubscript{2} on three ZIF structures with different topologies and compositions, including ZIF-8 (sodalite (SOD) topology), ZIF-76 (linde type A (LTA) topology) and ZIF-69 (gmelinite (GME) topology).

In view of large number of possible ZIFs, computational modeling techniques are quite instrumental in reliably predicting the structure, stability, and various adsorption and separation properties of ZIF materials.\textsuperscript{9-14,15,16} Rankin et al. computed adsorption of CO\textsubscript{2}, N\textsubscript{2}, CH\textsubscript{4}, and H\textsubscript{2} in ZIF-68 and ZIF-70 from atomistic simulations.\textsuperscript{17} Zhou and his coworkers used refined Optimized
Potentials for Liquid Simulations (OPLS) all atom force field (FF) model for grand canonical Monte Carlo (GCMC) simulations to investigate the H₂ adsorption sites at ZIF-8. Assfour et al studied hydrogen adsorption sites in ZIF-8, and -11 using molecular dynamics (MD) techniques with dispersion-corrected density functional based tight binding theory (DC-DFTB). Both Zhou et al. and Assfour et al. found that the primary H₂ adsorption sites are located close to the imidazolate ring, in proximity of the C=C bonds while the secondary H₂ adsorption sites are in the pore channel. Liu et al. evaluated the adsorption-based separation performance of ZIF-68, -69, for CO₂/N₂, CO₂/CH₄, and CH₄/N₂ mixtures. Liu and Smit employed refined Lennard-Jones (LJ) parameters based on UFF potential for frame atoms to simulate adsorption isotherms of CO₂, N₂, and CH₄ in ZIF-68 and ZIF-69. Their results matched well with experiments and demonstrated the influences of –Cl functional groups on the separation of gas mixtures.

However, in order to gain a more fundamental understanding and reliable predictions of the adsorption properties of various gas molecules on nanoporous materials, accuracy of ab initio methods are necessary. This is because gas adsorptions on ZIF materials are dominated by dispersion interactions. Although ab initio methods are computationally expensive, they result in relatively accurate interactions even for energetics of weak van der Waals (vdW) interactions. Düren and her co-workers directly used a density functional theory/coupled-cluster (DFT/CC) based potential energy surface implemented in GCMC simulations to predict the adsorption of methane in CuBTC (Copper 1,3,5-benzenetricarboxylate). Several ab initio based force fields have been developed for H₂, N₂, and CO₂ with various ZIFs. Goddard and coworkers reported H₂ uptake of various organic linkers with different ZIFs using high level ab initio based GCMC simulations. McDaniel et al. have developed physically motivated force field from Symmetry-Adapted Perturbation Theory (SAPT). The SAPT has the advantage that naturally
decomposes the interaction energy into the fundamental components of electrostatic, exchange, induction and dispersion interactions. In this last case, the force field could be used with polar fluids such as CO₂. Guo et al.\textsuperscript{29} investigated adsorption sites of ZIF-3 and ZIF-10 for CH₄ from GCMC simulations. Recently, Assfour et al.\textsuperscript{30} reported H₂ adsorption isotherm of various ZIFs (including ZIF-95) using first principles-based DFT with second-order Møller–Plesset perturbation (MP2) calculation and GCMC simulations. They found that the heat of adsorption of –Cl substituted and nitrogen heterocyles (pyrazine) linkers enhance the adsorption energy compared to the other ZIFs, which is in good agreement with experimental measurements.

\textbf{Figure 1.} Crystal structures of ZIF-95 and ZIF-100 along with their identical organic linker chlorobenzimidazole (cbIm), which is connected to two Zn atoms in the ZIF-95/100. Pictures are not drawn to scale. ZIF-100 has a much larger size and number of atoms compared to those of ZIF-95. C, N, O and Cl atoms are represented by gray, blue, red and green colors, respectively. H atoms are omitted for clarity. \textit{For simulations, the solvents (O atoms) are removed.}

Recently, Yaghi and coworkers synthesized ZIF-95, and -100 with exceptionally large and complex colossal cages as promising storage and separation porous materials for several gas mixtures.\textsuperscript{3} In the present study, we have focused on these functional group-based ZIFs, i.e. ZIF-95, and -100, for gas storage applications. Figure 1 shows ZIF-95, -100, which have an identical
linker, chlorobenzimidazole (cbIm), but different crystal structures. The latter are obtained from Crystallography data Centre (CCDC).\textsuperscript{31} We optimized the interactions of organic fragments and three gas molecules, H\textsubscript{2}, N\textsubscript{2}, and CH\textsubscript{4}, with different orientations by \textit{ab initio} based MP2 method. The results were then used to parameterize several Morse FF potentials for different atomic pairs. The Morse potentials were then incorporated into large-scale GCMC simulations to predict the adsorption capacity (both total and excess amount) and the heat of adsorption (Q\textsubscript{st}) of H\textsubscript{2}, N\textsubscript{2}, and CH\textsubscript{4} gases in ZIF-95 and ZIF-100. Our hierarchical multiscale approach rooted in the quantum level will not only abstract, capture and upscale the fundamental weak interactions associated with gas adsorptions in ZIFs, but also it offers an alternative economic way to laborious experimental works.

2. Computational methodology

2.1. \textit{Ab initio} Calculations to Develop Force Field Potentials for ZIF Models and Gases

In this study, cbIm moiety is a potential adsorption sites in ZIF-95 and ZIF-100. The interactions between various gas molecules (such as H\textsubscript{2}, N\textsubscript{2}, and CH\textsubscript{4}) and cbIm derivative (linker part in various ZIFs framework) are dominated by long-range London dispersion forces. \textit{We used MP2 method\textsuperscript{32} with 6-311++G** basis set for full geometry optimization. Next, we performed single point energy calculations at MP2/cc-pVTZ level of theory to quantify such weak interactions (except for H\textsubscript{2}···H\textsubscript{2} self-interactions, which was taken from earlier report using CCSD(T)/aug-cc-pVQZ method)\textsuperscript{33} and obtain the potential energy surfaces (PESs).} This level of theory includes electron correlation to the second order including London dispersion forces important to the interactions of gas molecules and organic models.\textsuperscript{34,35} To mimic the cbIm moiety, we have selected two simple organic molecules, benzene (BZ) and trichloro triazine (TC), interacting with guest molecules as presented in Figure 2. First, the optimum orientations
of organic linkers and gas molecules are obtained via *ab initio* calculations. Next, while the orientations were fixed, we found the minimum PES as a function of distance between the guest and host molecules. These PESs are much more accurate than the generic force field predictions for describing the vdW interactions between the guest and host molecules, and thus were used as benchmarks for fitting several Morse FF potentials. *This is because these PESs are obtained based on MP2/cc-pVTZ level of theory, suitable for quantifying weak vdW interactions, which are sensitive to local environments such as those in our study. Here, let’s remind that vdW interactions in generic force fields (e.g. UFF) are essentially not trained based on any particular environment, rather they are parameterized based on general intrinsic features of atoms, independent of the local environments (e.g. electron-electron correlations). Thus, while generic force fields are typically transferable to several environments, they are less accurate for any particular environment compared to the prediction of MP2/cc-pVTZ theory. As shown in Figure 3, we used a similar strategy with MP2/cc-pVTZ level of theory for calculating PESs for N\textsubscript{2} and CH\textsubscript{4} self-interactions. All *ab initio* calculations were performed using the Gaussian 09 suite of programs.*\textsuperscript{36}

**2.2. Force Field Parameters**

Using our high-level *ab initio* calculations, we developed several pair FF potentials to provide a proper description of the London dispersion forces responsible for the vdWds attractions. We used the Morse potential

\[ E = \left[ D \left(1 - \exp(-\alpha(r-r_0))\right) \right]^2 \] (1)
to model the pair interactions where the parameters $D$ (well-depth), $\alpha$ (well-width), and $r_0$ (Equilibrium distance) were fitted to the *ab initio* PES results. We obtained all the FF potential energies of the clusters by changing the internuclear distance between the gas-gas and gas-solid (e.g. N$_2$-Benzene) molecules. For instance, in view of the interactions of N$_2$ with Benzene in Figure 2a, the MP2/cc-pVTZ *ab initio* data for several internuclear distances ($r$) were fitted to the following expression to obtain the 6 independent Morse parameters for N-C and N-H interactions (3 for each type)

$$E_{\text{tot}} = \sum_{i=1}^{24} D_i \left( 1 - \exp \left( -\alpha_i \left(r - (r_0)_i\right) \right) \right)^2$$

(2)
Figure 2. Comparison of minimum potential energy surfaces (PESs) derived from first-principles and fitted Morse force field potentials for H₂ (a-b), N₂ (c-d) and CH₄ (e-f) gases on Benzene (BZ) and trichloro triazine (TZ). The orientation of non-spherical guest molecules is
important for obtaining minimum PESs. The favorable orientations were obtained prior to PES calculations.

Figure 3. Comparison of minimum potential energy surfaces (PESs) derived from first-principles and fitted Morse force field potentials for N₂ (a) and CH₄ (b) self-interactions.

Here, $i$ represent the individual guest-host atomic interactions involved in the N₂-Benzene cluster (the contributions of the self-interactions of Benzene and N₂ to total energy were subtracted by shifting the PES to zero at far internuclear distance between them). A Similar strategy was used to obtained the 6 Morse parameters for N-Cl and N-N interactions in Figure 2b (here the N-C interactions were substituted by the Morse parameters obtained from the Figure 2a). For the spherical CH₄ molecule, we considered all its 5 atoms as an effective specie centered at C, thus representing an “effective” potential for CH₄.

2.3. GCMC Simulation

We performed the GCMC simulations by using the fitted Morse Force field potentials obtained from the gas-gas and gas-solid interactions at MP2 level of theory. In this way, our approach eliminates the possible ambiguity and inaccuracies of GCMC simulations arising from
using the generic force fields.\textsuperscript{37} We used the parallelized version of Gulp code\textsuperscript{38} (Version 3.1) for all the GCMC calculations to quantitatively predict the gas adsorption isotherms under different thermodynamic conditions. In Gulp, the contributions of the long-range electrostatic forces are calculated using the Ewald summation technique.\textsuperscript{39} The GCMC simulations included one million ($10^6$) steps at the temperature 77 and 300 K for thermal equilibration. We implemented four types of trial moves in the Monte Carlo method: translation, insertion, deletion and rotation (for spherical molecules, i.e. CH$_4$, rotation was excluded). All the aforementioned trial moves had equal probability in our simulations. For the GCMC runs, the coordinates of ZIFs were fixed at their crystallographic positions and periodic boundary conditions were used to eliminate the boundary effects. We used cutoff distance of 10.0 Å for all the Morse FF potentials. Due to the large system sizes (specially in the case of ZIF-100), each adsorption point on the isotherm plots took approximately 3 days to be computed by using 96 parallelized CPUs. The Peng–Robinson equation of state (EOS)\textsuperscript{40} was used to relate the bulk experimental pressures to the chemical potential required in the grand canonical ensemble of the GCMC simulations. Absorption of ZIFs were quantified at increasing pressure intervals of up to 100 bar with small increments for pressures of less than 10 bar and coarser increments beyond 10 bar. We estimated the isosteric heats of adsorption ($Q_{st}$) by\textsuperscript{41}

\[ Q_{st} = RT - \left( \frac{\partial < V >}{\partial < N >} \right)_T \] (3)

where $R$ represents the gas constant, $<V>$ denotes the average potential energy of the adsorbed phase, and $<N>$ represents the average number of molecules adsorbed. The excess amount of adsorption were calculated by
where $V^g$ is the pore volume of the adsorbent and $\rho^g$ is the molar density of the bulk gas phase with Peng-Robison EOS.\textsuperscript{38} We used radial distribution functions (RDF) to examine the interactions between the gas molecules and the ZIFs framework.

3. Results and discussions

3.1. Optimization of Various Gas-ZIF Models and FF parameterization

From the optimized geometries of the selected models and gas molecules in Figure 2, we found that more stable conformations of H$_2$ molecule with the BZ (Figure 2a) and TZ (Figure 2b) clusters are perpendicular and parallel, respectively. However, in the case of N$_2$, the more stable orientations are reversed, i.e. parallel and perpendicular, for to BZ (Figure 2c) and TZ (Figure 2d) clusters owing to the different stereoelectronic nature of N$_2$-BZ/TZ (vs H$_2$-BZ/TZ) clusters. Due to the tetrahedral symmetry, methane molecule always orients such that an H atom is facing the BZ (Figure 2e) and TZ (Figure 2f) clusters. The stable orientations of the H$_2$ and CH$_4$ self-interactions with minimum energies are shown in Figure 3. By repeating the \textit{ab initio} calculations at different internuclear distances (with fixed orientations) and fitting, we obtained the full parameters of the Morse potentials for gas-gas and gas-solid (e.g. N$_2$-ZIF) interactions as shown in Table 1. Figure 2 and 3 show the close agreement of the fitted Morse potentials with our \textit{ab initio} data.

To validate the accuracy of our \textit{ab initio} based Morse potentials, we compared the results of a few representative GCMC simulations with available experimental data on CH$_4$ adsorption isotherm in ZIF-95 and -100 at 298 K and high pressure ranges. Figure 4 shows the good agreements between our calculated values of CH$_4$ adsorption isotherm on ZIF 95 and -100 at 298
K with experimental values. Additionally, our calculated H$_2$ adsorption isotherm and gravimetric density of ZIF-95 are in close agreement with earlier \textit{ab initio} based GCMC simulations.

Table 1. Morse Potential parameters used in the GCMC simulations to describe H$_2$, N$_2$, and CH$_4$ weak vdW interactions with ZIF as well as gas-gas self-interactions (for convenience, H$_2$, N$_2$, and CH$_4$ gas molecule are represented by H$_g$, N$_g$, and M$_g$, respectively).

<table>
<thead>
<tr>
<th>Interaction type</th>
<th>D (kcal/mol)</th>
<th>$r_0$ (Å)</th>
<th>α</th>
</tr>
</thead>
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<tr>
<td>H$_g$···H$_g$ $^a$</td>
<td>0.01815</td>
<td>3.5698</td>
<td>1.5000</td>
</tr>
<tr>
<td>H$_g$···Cl</td>
<td>0.17820</td>
<td>3.4307</td>
<td>2.6954</td>
</tr>
<tr>
<td>H$_g$···N</td>
<td>0.0500</td>
<td>3.0040</td>
<td>1.4691</td>
</tr>
<tr>
<td>H$_g$···C</td>
<td>0.1133</td>
<td>3.1912</td>
<td>1.6163</td>
</tr>
<tr>
<td>H$_g$···H</td>
<td>0.0018</td>
<td>3.2508</td>
<td>1.8927</td>
</tr>
<tr>
<td>N$_g$···N$_g$</td>
<td>0.1105</td>
<td>3.5936</td>
<td>1.7319</td>
</tr>
<tr>
<td>N$_g$···Cl</td>
<td>0.2959</td>
<td>4.2117</td>
<td>1.8862</td>
</tr>
<tr>
<td>N$_g$···N</td>
<td>0.1558</td>
<td>3.1779</td>
<td>1.9638</td>
</tr>
<tr>
<td>N$_g$···C</td>
<td>0.2452</td>
<td>3.1000</td>
<td>1.7144</td>
</tr>
<tr>
<td>N$_g$···H</td>
<td>0.0546</td>
<td>4.2804</td>
<td>1.8277</td>
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<tr>
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</tr>
<tr>
<td>M$_g$···H</td>
<td>0.0911</td>
<td>4.6534</td>
<td>1.8628</td>
</tr>
</tbody>
</table>

$^a$ H$_g$···H$_g$ potential taken from Ref. 33.
Figure 4. (a) Experimental and calculated CH$_4$ adsorption isotherm in ZIF-95 at 298K. (b) Experimental and calculated CH$_4$ adsorption isotherm in ZIF-100 at 298K. (Experimental values are taken from reference 3).

3. 3. H$_2$ Adsorption Isotherm of ZIF-95 and ZIF-100

Among different adsorption isotherms investigated in this work, only H$_2$ adsorption isotherm of ZIF-95 has been previously studied.$^{3,30}$ However, the H$_2$ adsorption isotherm of ZIF-100 and adsorption of other gases such as N$_2$, and CH$_4$ in both ZIF-95 and -100 are not yet reported. The collective adsorption studies of these gases into both ZIF-95 and -100 give valuable information about the uptake capacity of ZIFs at different isotherm conditions. Figure 5 shows the H$_2$ adsorption isotherms of ZIF-95 and -100 at 77 and 300 K at pressures of 1 to 100 bar, along with the previously reported *ab initio* studies on H$_2$. $^{30}$
Figure 5. (a) Calculated H\textsubscript{2} adsorption isotherms of ZIF-95 at 300 and 77K along with previously reported values taken from reference 30. (b) Calculated H\textsubscript{2} adsorption isotherms of ZIF-100 at 300 and 77K.

Figure 5a shows that H\textsubscript{2} uptake of ZIF-95 at 300 K and 1 bar is 0.03 wt\%. The adsorption capacity of ZIF-95 smoothly increases from 0.03 to maximum 0.9 wt\% when pressure increases from 1 to 100 bar. At 77 K, however, there is a rather sharp increase in adsorption from 1.7 to 2.4 wt\% when pressure changes between 1-10 bar. After this range, the increase in uptake relatively slows down with increase in pressure. The maximum adsorption capacity is \(~3.7\text{wt\%}\) at 100 bar, which is in close agreement with the earlier theoretical report.\textsuperscript{30} Overall, the H\textsubscript{2} adsorption capacity in ZIF-95 at 300 K (at all pressure range) is much less than that at 77 K.

A similar pattern is observed in H\textsubscript{2} adsorption capacity of ZIF-100. However, at low pressures (1-10 bar), the changes in uptake values at 300 K and 77 K in ZIF-100 are closer than those in ZIF-95 (see Figure 5b). The maximum uptake of ZIF-100 at 300 and 77 K at 100 bar is 3.4 and 10.5 wt\%, respectively. This is the first report on maximum H\textsubscript{2} adsorption capacity of
ZIF-100 at 77 K with 100 bar using *ab initio* based GCMC simulations. We find that the adsorption capacity of ZIF-95 and -100 at cryogenic temperature and 100 bar is about three times higher than those in room temperature, owing to the stronger gas-gas interactions at 77 K, and frozen state of rotational motion of gas molecules in this condition. Together, these factors lead to a tighter molecular arrangement, thus higher adsorption capacity at 77 K. Table 2 summarizes calculated maximum uptake of H₂, N₂, and CH₄ gases in ZIF-95 and -100 at 298 and 77 K temperatures.

**Table 2.** Calculated maximum uptake capacity of ZIF-95, ZIF100 at 300 and 77 K (and 100 bar) and comparison with Langmuir surface area.

<table>
<thead>
<tr>
<th>Gas</th>
<th>ZIF-95 (Surface Area 1240 m²/g)ᵇ</th>
<th>ZIF-100 (Surface Area 780m²/g)ᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300K 77K</td>
<td>300K 77K</td>
</tr>
<tr>
<td>H₂</td>
<td>0.9 3.7</td>
<td>3.4 10.5</td>
</tr>
<tr>
<td>N₂</td>
<td>13.1 18.5</td>
<td>7.5 19.8</td>
</tr>
<tr>
<td>CH₄</td>
<td>4.6 4.7 (5.2)ᵃ</td>
<td>3.2 2.8</td>
</tr>
</tbody>
</table>

ᵃMaximum uptake capacity observed at 77 k (80 bar).ᵇ Experimental value taken from Ref.3.

The calculated excess amount of H₂ adsorption from 1 to 100 bar at 300 and 77 K is presented in Table S1 in the supporting information (SI). The excess H₂ amount was calculated as the total amount of H₂ gas contained in the pores minus the amount of the gas that would be present in the pores in the absence of gas-solid intermolecular forces.⁴² Our results indicate that there is no significant difference between the total and excess H₂ adsorption capacity of ZIF-95 and -100 (only minor differences are observed in the pressure range of 10 to 100 bar).
3. 4. N\textsubscript{2} Adsorption Isotherms of ZIF-95 and ZIF-100

Figure 6 shows the N\textsubscript{2} adsorption isotherms of ZIF-95 and -100. Whereas ZIF-100 uptake at 300 K and 77 K as well as ZIF-95 uptake at 300 K increase gradually with respect to pressure, this is not the case for ZIF-95 uptake at 77 K. The latter shows no significant changes when pressure varies between 1 to 100 bar. Indeed, the N\textsubscript{2} uptake reaches to its maximum level at low pressures (1-10). This behavior may be better realized by considering the N\textsubscript{2} adsorption trend of ZIF-95 at higher temperature. At 300 K, the adsorption rapidly increases when the pressure changes from 1 to 10 bar, and then gradually increases at higher pressures. This suggests that the nature of interactions between N\textsubscript{2} molecules and ZIF-95 in conjunction with the pore volume and surface of the ZIF-95 are such that sufficiently small pressures, e.g. 1-10 bars, are enough to achieve the majority of the uptake capacity. More precisely, at 300 K, the rate of uptake is approximately 0.5 wt% per bar when pressure is 1-10 bar while this rate drops to 0.08 wt% per bar when pressure varies from 10 to 100 bar. At cryogenic temperature, due to special factors discussed earlier, this rate even becomes almost independent of the pressure variation. Table 2 shows the maximum N\textsubscript{2} adsorption capacity of both ZIF-95 and -100. At 77 K, the adsorption capacity of ZIF-95 and -100 are around 37\% and 250\% higher than those at room temperature, respectively. The excess and total amounts of N\textsubscript{2} adsorptions are presented in Table S2 in SI, indicating no significant differences between the two.
Figure 6. (a) Calculated N$_2$ adsorption isotherms of ZIF-95 at 300 and 77K. (b) Calculated N$_2$ adsorption isotherms of ZIF-100 at 300 and 77K.

3.5. CH$_4$ Adsorption Isotherm of ZIF-95 and ZIF-100

Figure 7 demonstrates the CH$_4$ adsorption isotherms of ZIF-95 and -100. In view of this Figure and Table 2, a few observations deserve particular attention. First, it is interesting to note that at 77 K, there are no significant changes in the adsorption capacity of ZIF-95 by increasing the pressure. This is reminiscent to the behavior and interactions previously discussed for N$_2$ adsorption at 77 K. Second, we find that the maximum CH$_4$ adsorptions of ZIF-100 at both 300 K and 77 K are smaller than those of ZIF-95 at similar temperatures. This is in contrast to the case of H$_2$ adsorption where ZIF-100 has a larger uptake capacity than ZIF-95 (see Table 2). We attribute this behavior to the smaller pore sizes of ZIF-100, which is able to accommodate smaller molecules (H$_2$) but not as quite efficient in adsorbing larger molecules (CH$_4$). Thus, although ZIF-100 may intuitively be expected to be a good storage material due to its larger
colossal structure than ZIF-95, our results indicate that ZIF-100 is more effective in storing small molecules. Earlier reports have also highlighted the critical role of pore size in adsorption.\textsuperscript{43}

Third, at high pressure (100 bar), the adsorption capacity of ZIF-95 at both 300 and 77 K are almost identical (4.6 versus 4.7 wt\%) while in ZIF-100, the adsorption capacity at 77 K is slightly lower than that in 300 K (2.8 vs 3.22\%). Furthermore, in the case of CH\textsubscript{4}, there are noticeable differences between the total and excess adsorptions at all isotherm conditions (see Table S3). For instance, the calculated excess adsorption capacity of ZIF-95 at 300 and 77 K is 4.2 (100 bar) and 4.9 wt\% (80 bar), respectively. The corresponding values for ZIF-100 at similar conditions are 3.0 and 2.6 wt\% (at 100 bar). We ascribe these behaviors to the effect of surface area and pore size as well as the size of the guest molecule, which will be discussed next.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figures.png}
\caption{(a) Calculated CH\textsubscript{4} adsorption isotherm of ZIF-95 at 300 and 77K. (b) Calculated CH\textsubscript{4} adsorption isotherm of ZIF-100 at 300 and 77K.}
\end{figure}
3.6. Comparison of Adsorption Capacity with Surface Area of ZIF-95 and ZIF-100

The experimentally measured Langmuir surface areas of ZIF-95 and ZIF-100 are 1240 and 780 m$^2$/g, with corresponding micropore volumes of 0.43 and 0.37 cm$^3$/g, respectively. We believe the adsorption capacity of ZIF-95 and -100 at high pressures depends on the competing effects of surface area/micropores and guest molecule size. The effect of surface area and pore volume at high pressures has been noted earlier. Here, we find that while the surface area influences the total available adsorption sites, the micropore volume and guest molecule size is important when it comes to self-interactions between guest molecules to take advantage of the available surface areas. On one hand, the uptake capacity of ZIF-100 outperforms ZIF-95 for small molecules such as H$_2$ even though both the surface area and micropore volumes of ZIF-100 are smaller than those of ZIF-95 (see Table 2). On the other hand, for large molecules such as CH$_4$, this trend reverses and ZIF-95 outperforms ZIF-100. This behavior is true at both 77 and 300 K. For molecules with a medium size in between H$_2$ and CH$_4$ (such as N$_2$), the behavior is more complex and strongly depends on the temperature. More precisely, at 77 K, the N$_2$ uptake capacity of both ZIF-95 and -100 are roughly equal (18.5 vs 19.8 wt%) while at 300 K, the uptake capacity of ZIF-95 is almost twice that of ZIF-100. Thus, our results clearly illustrate the competing role of the surface area (micropore volume) and the size of the guest molecule on maximizing the gas adsorption capacity. Figure S1-S3 further demonstrate the location of gas adsorption sites as a function of temperature.

3.7. Role of –Cl Functional Group on Gas Adsorption of ZIFs

Figure 8 shows the radial distribution function (RDF) between H$_2$, N$_2$, and CH$_4$ adsorbed gases and ZIF-95 at 77 K and 100 bar along with an atomistic snapshot of each system. As expected,
the gas molecules are not only adsorbed on the surface of ZIF-95, but also in the micropores, which is common in such high pressures. Via carefully analyzing the RDF plots, we infer that majority of such adsorptions in the microspores occur in the vicinity of the functional group present in the organic linker (cbIm). RDFs between hydrogen atoms of the H₂ gas molecules and host atoms of cbIm linker, i.e. C, N, H, and Cl atoms, are shown in Figure 8a. Similar RDFs are plotted in Figure 8b-c for N₂ and CH₄ molecules (in the case of CH₄, the center of mass of the methane molecules is considered for RDF calculations). Figure 8a-c indicates that the majority of gas adsorption occurs in the vicinity of the –Cl functional group of cbIm linker because of its high intensity of the RDFs around 3-4 Å compared to other atoms of the cbIM linker. In the cases of H₂ and N₂, we attribute this to the polar functional group of cbIm, which induces dipole interactions with H₂ and N₂ gas molecules. For H₂ gas molecules, this can be verified from the high energy well-depth of the Morse potential for Cl-H parameter (0.17820 kcal/mol) compared to those of other pair species (see Table 1). Similarly, high energy well-depth of the Cl-N parameter (0.2959) confirms this increased RDF peak.

However, in the case of CH₄ gases, the energy well-depth of the CH₄-Cl pair (0.1999 kcal/mol) is not the highest among the CH₄-ZIF interactions; it is second to the energy well-depth of CH₄-C pair (0.3636 kcal/mol). Thus, there must be another mechanism that lowers the high intensity of the RDF peak in the CH₄-C pair. A careful analysis of our fitted Morse potential parameters indicate that this is due to the competing mechanism of well-depth versus well-width in the Morse potential describing the essence of the interactions between the guest molecules and the cbIm linkers. This mechanism can be understood from the lower value of well-width (α=1.27) in the Morse Potential of CH₄-C pair compared to that of CH₄-Cl pairs (α=2.21). It is known that in the Morse potential, the lower the α, the higher the well width. Thus, although CH₄-C pair has a
higher well-depth than CH$_4$-Cl, its lower well-width with respect to CH$_4$-Cl causes the majority of the CH$_4$ adsorptions on C atoms not to be concentrated around the point where the well depth is maximum. This eliminates the probability of finding the maximum RDF peak around the equilibrium point with highest well-depth. The latter can be clearly seen from the smoothed out (blunt) RDF plot of CH$_4$-C pairs (the red plot in Figure 8c). This is in accord with other experimental and simulation studies on CH$_4$ adsorption at various ZIFs.$^{45}$ Our RDF analysis clearly reveals that functional group plays a significant role in adsorption capacity of ZIFs.

3. 8. Analysis of Isosteric Heat of Adsorption ($Q_{st}$) of Gases in ZIF-95 and ZIF-100

Isosteric heat of gas adsorption ($Q_{st}$) values in ZIFs were obtained from eq (1) during GCMC simulations. As an example, Figure 9 represents the simulated isosteric heat of adsorption for H$_2$, N$_2$ and CH$_4$ gases at both 300 and 77 K in ZIF-95. The calculated $Q_{st}$ values of all gases in ZIF-95 and -100 are shown in Table 3. For the H$_2$ gas at 300 K and high pressure (100 bar), both the ZIFs have the highest heat of adsorption when compared to 77 K. This is due to the high adsorption capacities of ZIFs at 77 K, which is three times higher than those at 300 K with identical pressures. In other words, the increased intermolecular interactions of gas molecules under cryogenic conditions reduce the $Q_{st}$ values. By increasing the pressure, the calculated $Q_{st}$ values of ZIFs are decreased because once the adsorption around the small apertures are saturated, the H$_2$ molecules are stored in the large pores (e.g. pores of 35.6 Å in ZIF-100). Here, it is notable that although the ZIF-95 has a higher $Q_{st}$ values than ZIF-100, it shows a lower H$_2$ uptake (~0.9 wt%) than ZIF-100 (3.4%) at 300 K. As discussed earlier, this goes back to the effect of surface areas and pore volumes in controlling the adsorption of small/large molecules.
Figure 8. Atomistic snapshots and radial distribution function (RDF) between H$_2$ (a), N$_2$ (b) and CH$_4$ (c) molecules and ZIF-95 framework at 77 K and 100 bar. The white, yellow, and red spheres represent the color of H$_2$, N$_2$, CH$_4$ gases, respectively.
The $Q_{st}$ values discussed so far were at high pressures. For instance, the calculated $Q_{st}$ values for CH$_4$ adsorption in ZIF-95 and -100 are 12.08 and 11.79 kJ/mol, respectively (at 100 bar and 77 K). At low pressure (1 bar) and 77 K, we found that these $Q_{st}$ values change to 15.66 and 20.33 kJ/mol, respectively. This is because of the higher adsorption capacity of ZIF-95 (1.93 wt%) than ZIF-100 (1.5 wt%) at 77K. Similar observations are found for other gases.

**Figure 9.** Calculated heats of adsorption values ($Q_{st}$ in kJ/mol) of H$_2$, N$_2$ and CH$_4$ gases in ZIF-95.

**Table 3.** Calculated isosteric heat of adsorption ($Q_{st}$) of H$_2$, N$_2$ and CH$_4$ gases at maximum adsorption capacity at 100 bar (in KJ/mol)

<table>
<thead>
<tr>
<th>Gas</th>
<th>ZIF-95</th>
<th>ZIF-100</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300K</td>
<td>77K</td>
</tr>
<tr>
<td>H$_2$</td>
<td>8.64</td>
<td>5.87</td>
</tr>
<tr>
<td>N$_2$</td>
<td>12.82</td>
<td>11.44</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>9.83</td>
<td>12.08</td>
</tr>
</tbody>
</table>
4. Conclusions

This work developed a hierarchical multiscale \textit{ab initio} based GCMC method to abstract, capture and upscale the fundamentals of H$_2$, N$_2$ and CH$_4$ gas adsorption behaviors of ZIF-95 and ZIF-100, as two porous nanomaterials with exceptionally large and complex colossal cages. By performing several \textit{ab initio} calculations on different orientations and internuclear distances \textit{via} MP2 level of theory, we obtained the minimum potential energy surfaces of various guest-host configurations in ZIFs. The latter enabled reliably extracting and developing several individual atom-atom interactions in the form of Morse pair potentials by which we performed large-scale GCMC simulations at various isotherm conditions. \textit{``This work provides important physical insights on the N$_2$ and CH$_4$ adsorption capacities of ZIF-95 and -100 using ab initio based GCMC simulations to better understand the effect of dipole-induced guest-host interactions, and steric and stereoelectronic effects in adsorption isotherms of ZIF''}. We found that while the adsorption capacity is typically larger at cryogenic temperatures than 300 K, there is a competing mechanism between surface area (pore volume) and the size of the guest molecule to maximize the uptake capacity. More precisely, we found that the uptake capacity of ZIF-100 outperforms ZIF-95 for small molecules such as H$_2$ even though both the surface area and micropore volumes of ZIF-100 are smaller than those of ZIF-95. However, for large molecules such as CH$_4$, this trend reverses and ZIF-95 outperforms ZIF-100. For molecules with a medium size such as N$_2$, the behavior is more complex and strongly depends on the temperature.

Equally important, our results reveal the gravimetric adsorption (both total and excess) density of H$_2$, N$_2$ and CH$_4$ in ZIF-95 and -100 at 77 K and 300 K. Interestingly, we calculated the maximum
H₂ adsorption capacity of ZIF-100 at 300 and 77 K (at 100 bar) to be 3.4 and 10.5 wt%, respectively. The former is quite close to the United States Department of Energy (DOE) 5.5% target for the H₂ storage capacity near room temperature by 2015.\textsuperscript{46} Functionalization of cbIm linker (e.g. alkali-doped cbIm) can potentially improve this capacity to meet the DOE target. Furthermore, our RDF analysis clearly reveals that –Cl functional group plays a vital role in the gas adsorption processes via inducing dipole interactions with guest molecules. Finally, we quantified the isosteric heat of adsorptions for all the studies gases at 77 and 300 K. Together, our results provide a rational computational framework with reliable \textit{ab initio} force field potentials (non-empirical) by which we can further study various properties of H₂, N₂ and CH₄ interactions with ZIF-95 and -100 systems (e.g. separation of binary CH₄/N₂ or ternary CH₄/N₂/H₂ gas mixtures) as well as interaction of these gases with other ZIF materials whose linkers possess similar composition to the cbIm linker, i.e. N, C, H, and Cl atoms.

\textbf{Acknowledgment}

The financial support by Rice University is greatly acknowledged. The supercomputer machines utilized in this work were supported in part by NIH award NCRR S10RR02950 and an IBM Shared University Research (SUR) Award in partnership with CISCO, Qlogic and Adaptive Computing, and in part by the Data Analysis and Visualization Cyber infrastructure funded by NSF under grant OCI-0959097.

\textbf{Supporting Information}
Gas adsorption sites and detailed information of total and excess H₂, N₂ and CH₄ gas adsorptions in ZIF-95 and -100. This material is available free of charge via the Internet at http://pubs.acs.org.

References


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