

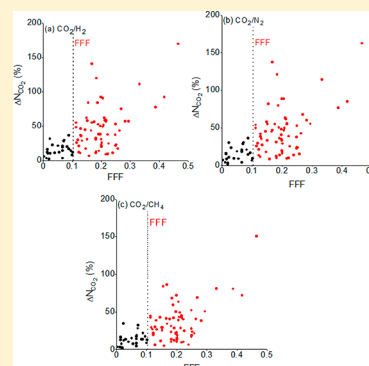
Effects of Force Field Selection on the Computational Ranking of MOFs for CO₂ Separations

Derya Dokur and Seda Keskin*[✉]

Department of Chemical and Biological Engineering, Koc University, Rumelifeneri Yolu, Sariyer, 34450 Istanbul, Turkey

Supporting Information

ABSTRACT: Metal–organic frameworks (MOFs) have been considered as highly promising materials for adsorption-based CO₂ separations. The number of synthesized MOFs has been increasing very rapidly. High-throughput molecular simulations are very useful to screen large numbers of MOFs in order to identify the most promising adsorbents prior to extensive experimental studies. Results of molecular simulations depend on the force field used to define the interactions between gas molecules and MOFs. Choosing the appropriate force field for MOFs is essential to make reliable predictions about the materials' performance. In this work, we performed two sets of molecular simulations using the two widely used generic force fields, Dreiding and UFF, and obtained adsorption data of CO₂/H₂, CO₂/N₂, and CO₂/CH₄ mixtures in 100 different MOF structures. Using this adsorption data, several adsorbent evaluation metrics including selectivity, working capacity, sorbent selection parameter, and percent regenerability were computed for each MOF. MOFs were then ranked based on these evaluation metrics, and top performing materials were identified. We then examined the sensitivity of the MOF rankings to the force field type. Our results showed that although there are significant quantitative differences between some adsorbent evaluation metrics computed using different force fields, rankings of the top MOF adsorbents for CO₂ separations are generally similar: 8, 8, and 9 out of the top 10 most selective MOFs were found to be identical in the ranking for CO₂/H₂, CO₂/N₂, and CO₂/CH₄ separations using Dreiding and UFF. We finally suggested a force field factor depending on the energy parameters of atoms present in the MOFs to quantify the robustness of the simulation results to the force field selection. This easily computable factor will be highly useful to determine whether the results are sensitive to the force field type or not prior to performing computationally demanding molecular simulations.



1. INTRODUCTION

Metal organic frameworks (MOFs), composed of organic linkers connected by metal cations, offer high porosities, large surface areas, and good mechanical and chemical stabilities.^{1–3} These attractive physical and structural properties make MOFs strong alternatives to traditional adsorbents for CO₂ capture.⁴ Several studies investigated adsorption-based CO₂ separation performances of MOFs.^{5–8} A comparison of different porous adsorbents including MOFs, zeolites, and activated carbons shows that MOFs can outperform zeolites and carbon-based adsorbents due to their high CO₂ selectivities and working capacities.⁹ Combining various metals and organic linkers, thousands of MOFs have been synthesized to date with a large variety in geometries and chemical properties. Large numbers of MOFs offer both an opportunity and a challenge: It can be possible to find an ideal MOF adsorbent for a target CO₂ separation process due to the availability of many different materials. However, testing thousands of MOFs using purely experimental techniques at the lab scale is simply impractical. Molecular simulations have been successful to provide atomistic insights into gas adsorption and gas separation in MOFs. One of the contributions of molecular simulations is to screen a large number of MOFs in a time-effective manner to identify the most promising materials for desired applications to guide

the experimental efforts, time, and resources to these promising materials.^{10–13}

The main and perhaps the most important input of molecular simulations of MOFs is a set of equations and parameters describing the physical and chemical interactions between gas molecules and MOFs. These equations and parameters together are known as force fields (FFs). The accuracy of a simulation strongly depends on the choice of the FF that describes gas-material interactions. Therefore, using accurate FFs in molecular simulation of materials is essential to make reliable predictions about the materials' performances. At the early stages of the molecular simulation studies of MOFs, efforts have been made to develop new FFs specific to gas–MOF interactions using quantum-level calculations.^{14,15} These calculations are computationally demanding; therefore, they can be performed for a very small number of MOFs but not for large-scale screening of materials. Some studies refined the generic FF parameters to better match the predictions of molecular simulations with the available experimental measure-

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ments of gas adsorption in MOFs.^{16,17} However, experimental studies focused on a small group of materials among thousands of available MOFs and many materials are lacking the experimentally measured gas adsorption isotherm data that can be used to validate the FF.

Due to these reasons, it is challenging and computationally very demanding to develop a new FF applicable to all kinds of MOFs. As a result, two off-the-shelf, generic FFs, Universal Force Field (UFF)¹⁸ and Dreiding,¹⁹ are very widely used in molecular simulations of MOFs. Several studies compared the results of molecular simulations employing either UFF or Dreiding with the experimentally measured gas uptake data of MOFs and showed good agreement between experiments and simulations, validating the usage of these two FFs for MOFs.¹⁰ The CO₂ adsorption isotherms of 424 hypothetical MOFs were recently computed using both the UFF and an *ab initio* FF.²⁰ Results showed that there are significant quantitative differences between the CO₂ uptakes predicted by the generic FF and the *ab initio* FF. In spite of these quantitative differences in CO₂ uptakes, a good correlation was reported between the relative rankings of MOFs in terms of absolute CO₂ uptake capacities predicted by different FFs. It was concluded that it may be a reasonable approximation to employ UFF in identifying the top percentage of MOFs for a particular gas adsorption application, but caution is still warranted. At that point, it is important to note that there are also examples of where UFF and Dreiding may fail in predicting gas adsorption data of MOFs. For example, Smit's group²¹ reported that common FFs typically underestimate the CO₂ adsorption in Mg-MOF-74, which has open metal sites, and presented a novel methodology that gives accurate FFs for CO₂ and N₂ adsorption in this MOF from high-level quantum chemical calculations. These FFs were defined to account for the subtle changes in the chemical environment induced by the presence of open metal sites in MOFs. Boyd et al.²² recently evaluated the bulk properties of several MOFs using generic FFs and showed that UFF and Dreiding provide good values for the bulk modulus and linear thermal expansion coefficients of these materials. FFs that are specifically developed for MOFs such as UFF4MOF were also reported to provide accurate values for these materials' properties. They concluded that each FF offers a moderately good picture of these properties.

The role of FF selection on the predicted mixture adsorption in MOFs can be much more important than the one on the single-component gas uptake because of the competitive interactions between different gas species of a mixture for the same adsorption site of a MOF. Dreiding and UFF have been commonly used in large-scale screening of MOF adsorbents. For example, Watanabe and Sholl²³ used Dreiding in their molecular simulations and reported the CO₂/N₂ selectivity of 359 MOFs. Wu et al.²⁴ studied separation of CO₂/N₂ mixtures in 105 MOFs using Dreiding. Qiao et al.²⁵ recently reported a molecular simulation study that employs UFF to study MOFs for CO₂ separation from flue gas and natural gas. We recently performed molecular simulations to compute adsorption-based CO₂/H₂, CO₂/N₂, and CO₂/CH₄ separation performances of 100 representative MOFs.²⁶ In our simulations, UFF was used for 28 MOFs, and Dreiding was employed for 72 MOFs based on the agreement between the simulation results and available experimental gas uptake data of MOFs. These MOFs were then ranked using several adsorbent performance evaluation metrics such as selectivity and regenerability which were calculated using the mixture adsorption data obtained from the molecular

simulations. However, the impact of FF type on the predicted gas separation performances of MOF adsorbents and their rankings has not been explored to date. Considering the ongoing research on high-throughput molecular simulations of MOFs for adsorption and separation of various gas mixtures, it is important to examine the robustness of adsorbents rankings with respect to the FF type.

In this work, we performed molecular simulations to compare the results from two different generic FFs, Dreiding and UFF, by computing adsorption of CO₂/H₂, CO₂/N₂, and CO₂/CH₄ mixtures in 100 different MOF structures. Using the gas adsorption data, four adsorbent evaluation metrics, adsorption selectivity, working capacity, sorbent selection parameter, percent regenerability were computed for each MOF and for each gas separation. The metrics obtained from molecular simulations using different FFs were first compared to understand their sensitivities to the FF type. MOFs were then ranked based on these performance evaluation metrics to identify the top 10 best materials for separation of CO₂/H₂, CO₂/N₂, and CO₂/CH₄ mixtures. The MOFs that appear in the highly promising materials list of Dreiding and UFF-based molecular simulations were compared and the robustness of the material rankings with respect to the FF type was discussed. At that point, it is important to note that we did not intend to examine the accuracy of these FFs, because both Dreiding and UFF were previously used to predict the CO₂ uptakes of various MOFs and comparison with the experimentally measured gas adsorption data showed that both are good in capturing the adsorption isotherms.^{26,27} We mainly aimed to define "a safe region" for MOFs in which using either Dreiding or UFF will not lead to significantly different results about the gas separation performance of a material. With this motivation, we proposed a force field factor, depending on the number and type of the atoms present in the MOF and their corresponding energy parameters. We showed that if this easily computable factor is low then either the Dreiding or UFF can be used to estimate the CO₂ uptake and CO₂ separation performance of the MOF. This factor will be highly useful to guide the simulators about the sensitivity of the predictions for the CO₂ uptake of MOFs to the FF type prior to performing computationally demanding molecular simulations.

2. COMPUTATIONAL DETAILS

We considered the same 100 MOFs that were studied in our previous work²⁶ to have a representative structural database that spans a wide range of chemical functionalities. Crystal structures of all MOFs were taken from the Cambridge Crystallographic Data Centre (CCDC).²⁸ The complete list of the materials with CCDC names and structural properties such as pore limiting diameter (PLD), largest cavity diameter (LCD), pore volume, porosity, and surface area of the MOFs can be also found in our previous report.²⁶ We used Grand Canonical Monte Carlo (GCMC)²⁹ simulations to compute adsorption isotherms of binary gas mixtures, CO₂/H₂, CO₂/N₂, and CO₂/CH₄ in MOFs. In a GCMC simulation, adsorbed amounts of each gas component were calculated by specifying the bulk pressure, temperature, and composition of the bulk gas mixtures. Five different types of moves were considered for GCMC simulations of gas mixtures including translation, rotation, insertion, deletion, and exchange of molecules. The Lorentz–Berthelot mixing rules were employed. The cutoff distance for truncation of the intermolecular interactions was set to 13 Å. Periodic boundary conditions were applied in all

simulations. A simulation box of $2 \times 2 \times 2$ crystallographic unit cells was used. During the simulations, 1.5×10^7 steps were performed to guarantee the equilibration and 1.5×10^7 steps were performed to sample the desired properties. Rigid framework assumption was used in all simulations following the literature^{30–32} and the good agreement between the results of simulations using rigid framework and the experimentally measured gas adsorption data was shown in our previous work.²⁶

Molecular simulations were first performed using Dreiding and then repeated under the same conditions using the UFF. These two FFs are widely used in simulations of MOFs for gas adsorption because they offer the advantage of being adaptable to many chemical environments. Dreiding is a generic FF developed back in 1990 to predict structures and dynamics of organic, biological, and main group inorganic molecules.¹⁹ UFF was introduced in 1992 as a full periodic table FF where the parameters were estimated using general rules based on the element, its hybridization and its connectivity.¹⁸ For some metal atoms of the MOFs, such as Ag, Be, Cd, Co, Cu, Fe, Mn, Nd, Ni, and Zr, potential parameters are not available in the Dreiding FF. These parameters were taken from the UFF. Potential parameters of the MOF atoms in UFF and Dreiding are given in Table S1. It is important to note that we showed very good agreement between our simulation results and experimentally measured CH₄, H₂, N₂, and CO₂ adsorptions in many MOFs in our previous works.^{26,33,34} For example, we showed the accuracy of our simulations by comparing simulated CH₄ adsorption of MOFs with 267 experimental data at a variety of pressures and temperatures.³³ Similarly, the good agreement between simulated H₂ adsorption and the experimentally reported data of a variety of MOFs including many subfamilies such as IRMOFs, PCNs, and ZIFs was shown.³⁴ Good agreements between experimental and simulated data of CO₂ adsorption in a large number of MOFs such as IRMOF-1, IRMOF-3, MOF-14, ZIF-8, ZIF-68, ZIF-79, CuBTC was shown in our recent work.²⁶ We also demonstrated the good agreement between experimentally reported CO₂/CH₄, CO₂/N₂ and CO₂/H₂ selectivities of various MOF groups including IRMOFs, ZIFs, MILs, MOF-74 series and our simulation data in Figure S1 to validate the accuracy of our molecular simulations in estimating the MOF adsorbents' selectivities.

Gas molecules were modeled using Lennard-Jones (LJ) potentials. A three-site rigid molecule with LJ 12–6 potential was used to model CO₂ and locations of the partial point charges were set as center of each site.³⁵ N₂ was also modeled as a three-site molecule: Two sites were located at the N atoms, and the third site was located at the center of the mass with partial point charges.³⁶ H₂³⁷ and CH₄³⁸ were modeled by using single-site spherical LJ 12–6 potentials. Electrostatic interactions were taken into consideration using the Coulomb potential for gas molecules with multipole moments, CO₂ and N₂. The cutoff distance for truncation of electrostatic interactions was set to 25 Å. In order to compute the electrostatic interactions between gas molecules and MOFs, partial point charges were assigned to MOF atoms using extended charge equilibration method (EQeq).³⁹ A recent study examined the impact of atomic charge assignment methods of MOFs on the high-throughput computational screening for CO₂/H₂O separations and found that the majority of the top MOFs are identical regardless of the charge assignment method.⁴⁰

Adsorption data of gas mixtures obtained from the GCMC simulations were used to compute several adsorbent evaluation metrics, namely adsorption selectivity (*S*), working capacity (ΔN), sorbent selection parameter (*S*_{sp}), and percent regenerability (*R*%). Calculation details of these metrics are given in Table 1. In these equations, *x*(*y*) represents the

Table 1. Adsorbent Evaluation Metrics Used in Ranking of MOFs

metrics	calculation
selectivity	$S_{\text{ads}(1/2)} = \frac{x_1/x_2}{y_1/y_2}$
working capacity (mol/kg)	$\Delta N = N_{\text{ads}} - N_{\text{des}}$
sorbent selection parameter	$S_{\text{sp}} = \frac{(S_{\text{ads}(1/2)})^2}{(S_{\text{des}(1/2)})^2} \times \frac{\Delta N_1}{\Delta N_2}$
percent regenerability (%)	$R\% = \frac{\Delta N_1}{N_{1,\text{ads}}} \times 100\%$

compositions of the adsorbed (bulk) gases in the adsorbent, and *N*_{ads} and *N*_{des} are the gas uptakes at the adsorption and desorption pressures, respectively. Subscript 1 (2) represents strongly (weakly) adsorbed gas. In our study, component 1 is always CO₂ and component 2 is either H₂, N₂, or CH₄ depending on the mixture. All calculations were performed at an adsorption pressure of 1 bar and desorption pressure of 0.1 bar at 298 K. Compositions of the binary gas mixtures were set as CO₂/H₂: 15/85, CO₂/N₂: 15/85, and CO₂/CH₄: 50/50 in molecular simulations to mimic industrial operating conditions. The operating conditions and gas compositions were specifically chosen to represent the landfill gas separation (CO₂/CH₄) and flue gas separation (CO₂/N₂) using vacuum swing adsorption following the literature.⁴¹

3. RESULTS AND DISCUSSION

Selectivity is generally considered as the primary metric in ranking adsorbent materials. An adsorbent with high selectivity is accepted as promising in gas separation applications. Therefore, we first computed selectivities of MOFs for CO₂/H₂, CO₂/N₂, and CO₂/CH₄ mixtures at 1 bar and 298 K using the mixture adsorption data obtained from the GCMC simulations. The CO₂ selectivities of MOFs computed from molecular simulations employing Dreiding and UFF are compared in Figure 1 for three gas mixtures. Comparison of selectivities obtained from two sets of molecular simulations using different FFs is also separately given for CO₂/H₂, CO₂/N₂, and CO₂/CH₄ mixtures in Figures S2–S4, respectively. The CO₂ selectivities calculated with Dreiding (UFF) are in the ranges of 10.48–2237.35 (12.38–3119.09), 3.73–202.30 (3.75–197.48), and 1.66–59.38 (1.71–60.97) for CO₂/H₂, CO₂/N₂, and CO₂/CH₄ mixtures, respectively. Figure 1 shows that molecular simulations with UFF led to slightly higher selectivities for CO₂/H₂ mixtures compared to the ones with Dreiding. Selectivities calculated for CO₂/N₂ and CO₂/CH₄ mixtures were similar for most MOFs regardless of the FF type. In extreme cases, using UFF can give 2.2, 1.6, and 1.7 times larger CO₂/H₂, CO₂/N₂, and CO₂/CH₄ selectivities than using the Dreiding FF. For example, CO₂/H₂ selectivity of a MOF, LASPOM, was predicted as 205.59 by Dreiding and 441.25 by UFF, leading to a large difference of 114.63%. The largest deviations for CO₂/N₂ and CO₂/CH₄ selectivities were

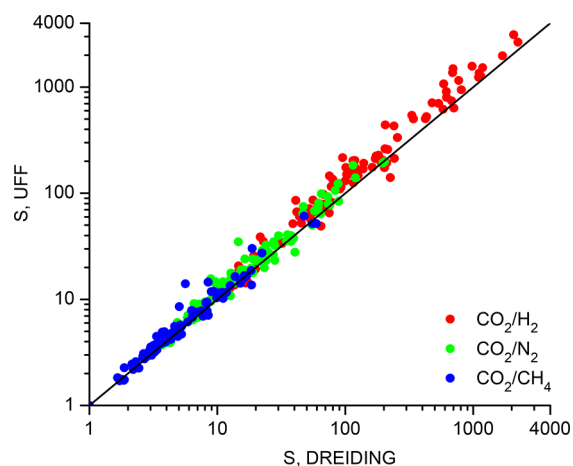


Figure 1. Comparison of selectivities of MOFs computed using Dreiding and UFF for CO₂/H₂, CO₂/N₂, CO₂/CH₄ separations. Diagonal line is to guide the eye.

observed for OCIZIL and LUXDEO, respectively. The CO₂/N₂ (CO₂/CH₄) selectivity of the relevant MOF was predicted as 47.00 (8.45) by Dreiding and 75.10 (14.54) by UFF, resulting in 59.77% (71.97%) difference. The discrepancies originated from using different FFs can be explained with the changes in the energy parameters of MOF atoms. For example, OCIZIL has Zn as the metal atom and the energy parameter of

Zn significantly increases when the UFF was used instead of Dreiding ($\epsilon_{\text{Zn,Dreiding}}/k_{\text{B}} = 27.69$ K, $\epsilon_{\text{Zn,UFF}}/k_{\text{B}} = 62.44$ K) in simulations. As a result, adsorption of CO₂ increases and more pronounced deviations are observed for the CO₂ selectivity. Overall, Figure 1 shows that both Dreiding and UFF can be used in the molecular simulations for the initial screening of MOF adsorbents based on selectivity, however caution is advised especially for CO₂/H₂ mixtures where the selectivity predictions of Dreiding and UFF may significantly vary. At that point, it is important to note that the MOFs we considered in this work have metal atoms of Ag, Al, Be, Cd, Co, Cu, Fe, In, Mn, Nd, Ni, V, Zn, and Zr. Among these, Al, In, and Zn have different energy parameters in Dreiding and UFF. The change in the energy parameters of Zn is the highest as can be seen from Table S1. For example, the energy parameters of In in the UFF and Dreiding are very close ($\epsilon_{\text{In,Dreiding}}/k_{\text{B}} = 276.96$ K, $\epsilon_{\text{In,UFF}}/k_{\text{B}} = 301.63$ K). Although there are changes in the energy parameters, the correlation coefficients (R^2) between the predictions of Dreiding and UFF for the selectivities of MOFs containing Al, In, and Zn were computed to be not very different (0.97, 0.95, and 0.89 for CO₂/H₂, CO₂/N₂, and CO₂/CH₄ mixtures, respectively) than the R^2 values (0.96, 0.94, and 0.94 for CO₂/H₂, CO₂/N₂, and CO₂/CH₄ mixtures, respectively) computed for MOFs that contain other metals.

Since selectivity solely depends on the gas uptakes of MOFs, we examined the role of the FF type on the gas uptakes of MOFs. Among the four gases we considered, CO₂ is the most

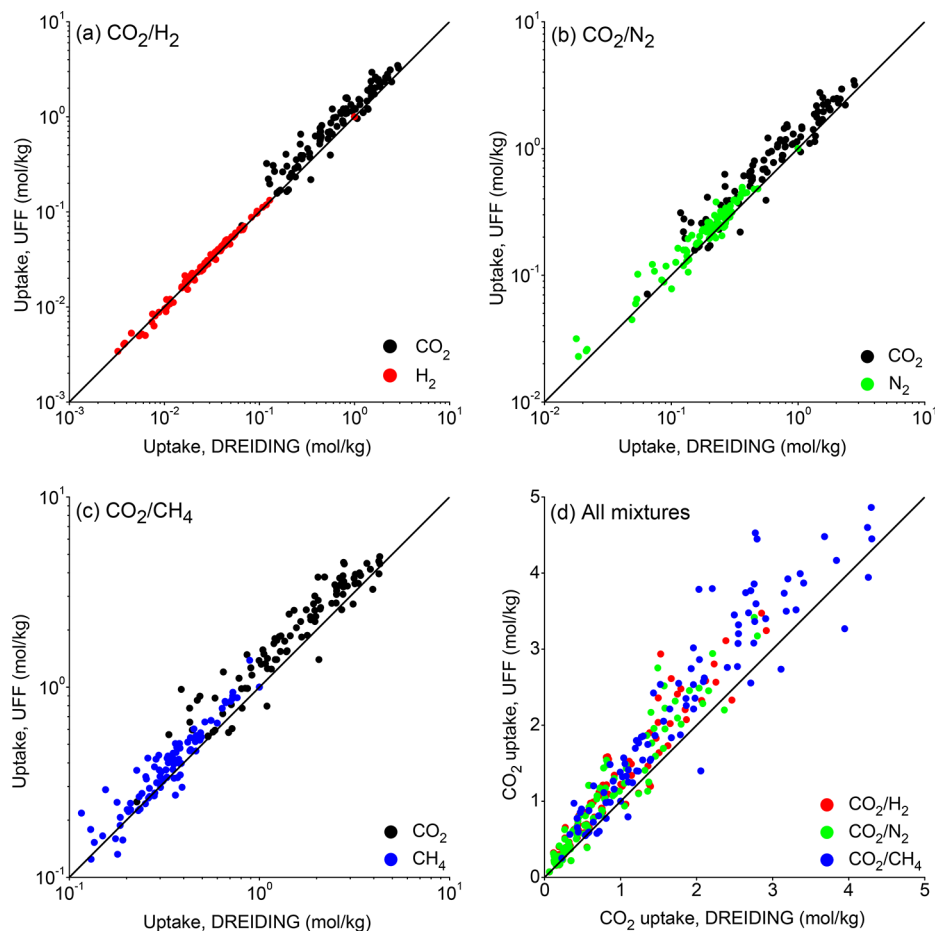


Figure 2. Comparison of gas uptakes of MOFs computed using Dreiding and UFF for (a) CO₂/H₂, (b) CO₂/N₂, (c) CO₂/CH₄, and (d) all mixtures. Diagonal lines are to guide the eye.

Table 2. Correlation Coefficients (R^2) for the Gas Uptakes Predicted by Dreiding and UFF

	CO ₂ uptake (mol/kg)		H ₂ uptake (mol/kg)		N ₂ uptake (mol/kg)		CH ₄ uptake (mol/kg)	
	0.1 bar	1 bar	0.1 bar	1 bar	0.1 bar	1 bar	0.1 bar	1 bar
CO ₂ /H ₂	0.9419	0.9177	0.9914	0.9952				
CO ₂ /N ₂	0.9403	0.9179			0.9268	0.9136		
CO ₂ /CH ₄	0.9408	0.8813					0.8404	0.9293

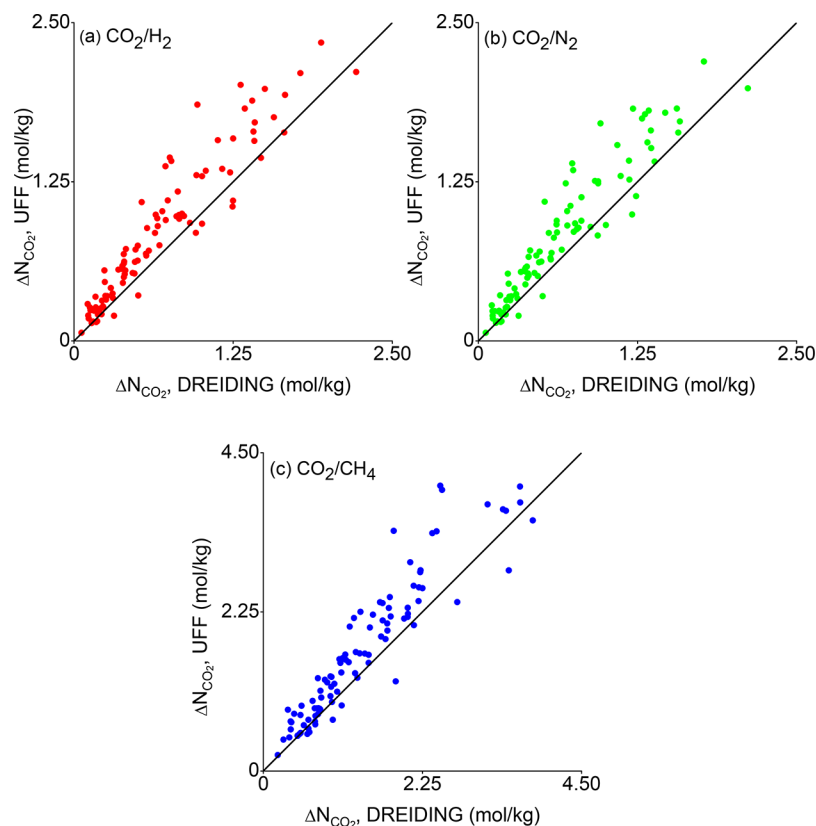


Figure 3. Comparison of the CO₂ working capacities of MOFs computed using Dreiding and UFF for (a) CO₂/H₂, (b) CO₂/N₂, and (c) CO₂/CH₄ mixtures. Diagonal lines are to guide the eye.

strongly adsorbed component. It was represented as a three-site molecule which has more interactions sites with the MOF atoms compared to other gases in addition to the electrostatic interactions due to its quadrupole moment. H₂ has very weak interactions with MOFs leading to very low uptakes. Figure 2 shows that molecular simulations performed at 1 bar using UFF generally result in higher uptakes for CO₂, CH₄ and N₂ compared to the ones performed using Dreiding. This result is more pronounced for CO₂, followed by CH₄ and N₂, as can be seen in Figures S5–S7 where uptakes for each gas species are separately shown. The CO₂ uptakes of MOFs for CO₂/H₂, CO₂/N₂, and CO₂/CH₄ mixtures were computed as 0.07–2.92 (0.07–3.47), 0.06–2.80 (0.07–3.42), and 0.23–4.30 (0.25–4.86) mol/kg, respectively using the Dreiding (UFF). The H₂ uptakes of MOFs were calculated to be almost same, 0.003–0.13 mol/kg, regardless of the FF type. The correlation coefficient (R^2) was defined as a linear fit between the Dreiding predicted results and UFF predicted results. The R^2 between the predictions of Dreiding and UFF for the gas uptakes of MOFs computed at 1 bar are given in Table 2. The R^2 values also show that CO₂ is the component which is more sensitive to the FF type, followed by N₂ and CH₄, whereas H₂ uptakes do not change with the FF. Since UFF-based simulations

overpredicted the N₂ and CH₄ uptakes of MOFs in similar amounts compared to the CO₂ uptake, CO₂/N₂ and CO₂/CH₄ selectivities predicted by two FFs were not significantly different as previously shown in Figure 1. The CO₂ uptakes predicted by UFF were higher than those of Dreiding but almost same for H₂. As a result, UFF-based simulations give much larger CO₂/H₂ selectivities than those of the Dreiding-based ones. These results indicate that the more strongly adsorbed component in MOFs, in our case CO₂, is more sensitive to the type of the FF used in the simulations compared to the weakly adsorbed gases. In other words, if the adsorption competition between two gas molecules is low, such as CO₂ and H₂, then selectivities predicted by two different FFs can be significantly different.

Working capacity is generally considered as the second most important metric used to evaluate new adsorbent materials. Figure 3 represents the predicted CO₂ working capacities of MOFs at an adsorption pressure of 1 bar and desorption pressure of 0.1 bar. Detailed comparison of CO₂ uptakes of MOFs at 0.1 and 1 bar using Dreiding and UFF can be found in Figures S8–S10 for all three mixtures. Similar to the CO₂ uptakes, CO₂ working capacities predicted by UFF generally overestimated the predictions of Dreiding. Table 3 shows that

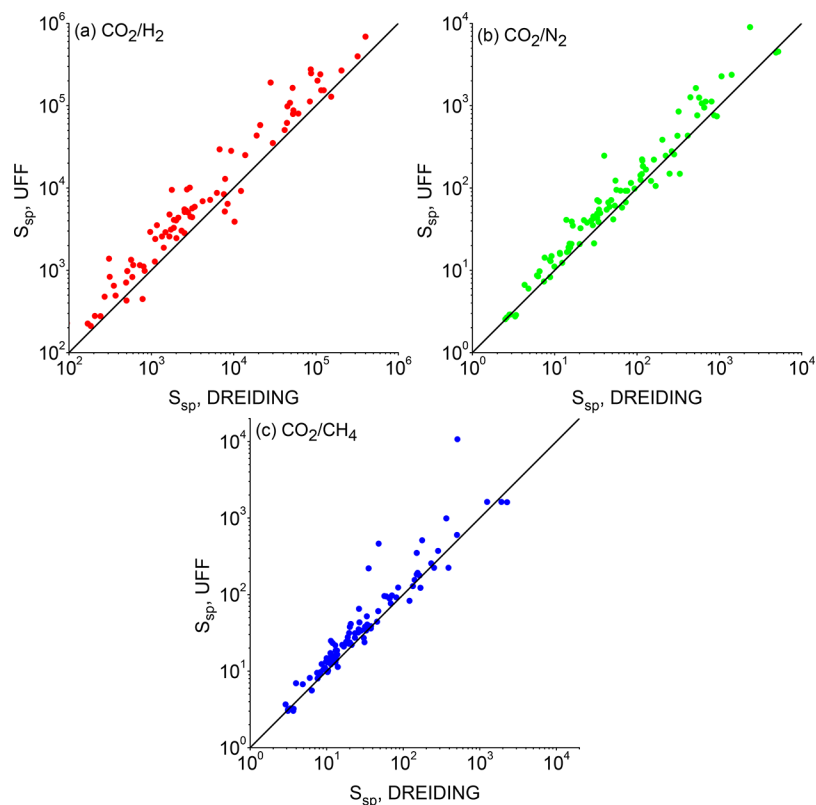
Table 3. Correlation Coefficients (R^2) for the Performance Evaluation Metrics Predicted by Dreiding and UFF for Each Gas Mixture

	S	ΔN_{CO_2} (mol/kg)	S_{sp}	R%
CO ₂ /H ₂	0.9528	0.8928	0.9674	0.9378
CO ₂ /N ₂	0.9434	0.8936	0.9552	0.9377
CO ₂ /CH ₄	0.9408	0.8648	0.9105	0.9549

R^2 values of the working capacities (0.86–0.89) are lower than those of selectivities (0.94–0.95), indicating that working capacity is much more sensitive to the FF type than the selectivity. Combining selectivity and working capacity in a single parameter, S_{sp} is useful to easily identify the most promising adsorbents. We compared S_{sp} values of MOFs using the results of simulations employing Dreiding and UFF in Figure 4. The S_{sp} values of MOFs for CO₂/H₂, CO₂/N₂, and CO₂/CH₄ separations were calculated as 19.34– 3.9×10^5 (26.74 – 6.9×10^5), 2.51–5178.36 (2.54–8980.72), and 2.91–2276.69 (3.02 – 1.07×10^4), respectively using the Dreiding (UFF). These numbers indicate that quantitative predictions of molecular simulations for S_{sp} strongly depend on the FF type. This is in fact a natural result of the mathematical description of S_{sp} . It includes the square of the selectivity, and as we discussed in Figure 1, there are several MOFs for which UFF-based simulations predicted double of the CO₂ selectivities compared to the Dreiding-based simulations. As a result, there are MOFs for which using UFF gives 1.73, 1.73, and 4.70 times higher S_{sp} values than using Dreiding for CO₂/H₂, CO₂/N₂, and CO₂/CH₄ separations, respectively.

We finally examined the impact of FF on the predicted percent regenerabilities ($R\%$) of MOFs. Although MOF adsorbents are used to be ranked based on selectivity, our recent study showed that it is much more efficient to screen MOFs based on $R\%$ because a large number of MOFs having high CO₂ selectivities suffers from very low $R\%$ (<75%).²⁶ Figure 5 shows that $R\%$ of MOFs ranges from 48.83 to 90.64% (44.32–91.12%) for CO₂/H₂ separation based on the molecular simulations performed using Dreiding (UFF). $R\%$ is defined as the ratio of working capacity to the gas uptake at an adsorption pressure. Since overestimation of UFF for CO₂ uptake is higher than the one for the CO₂ working capacity, $R\%$ predictions of UFF are generally lower than those of Dreiding. $R\%$ of MOFs ranges from 46.32 to 90.47% (33.52–91.48%) for CO₂/N₂ (CO₂/CH₄) separation based on the molecular simulations performed using Dreiding whereas UFF results are slightly less, 44.39–90.83% (26.37–91.68%). Similar to the selectivity, the R^2 values for $R\%$ (0.94–0.95) are high, as shown in Table 3, although sometimes large quantitative deviations were observed in the predicted $R\%$ values from two different FFs.

R^2 values calculated for all the adsorbent evaluation metrics can be seen in Table 3. The R^2 values are high (>0.86) for all four metrics suggesting that both FFs make quantitatively similar estimates for the four performance evaluation metrics that we discussed. Therefore, we also examined how the rankings of best MOF adsorbents change with Dreiding and UFF. The top 10 MOFs rankings based on the four performance evaluation metrics computed from two different FFs are listed in Table 4. According to the CO₂/H₂ selectivity ranking, there are 8 common MOFs in the top promising

**Figure 4.** Comparison of sorbent selection parameters of MOFs computed using Dreiding and UFF for (a) CO₂/H₂, (b) CO₂/N₂, and (c) CO₂/CH₄ mixtures. Diagonal lines are to guide the eye.

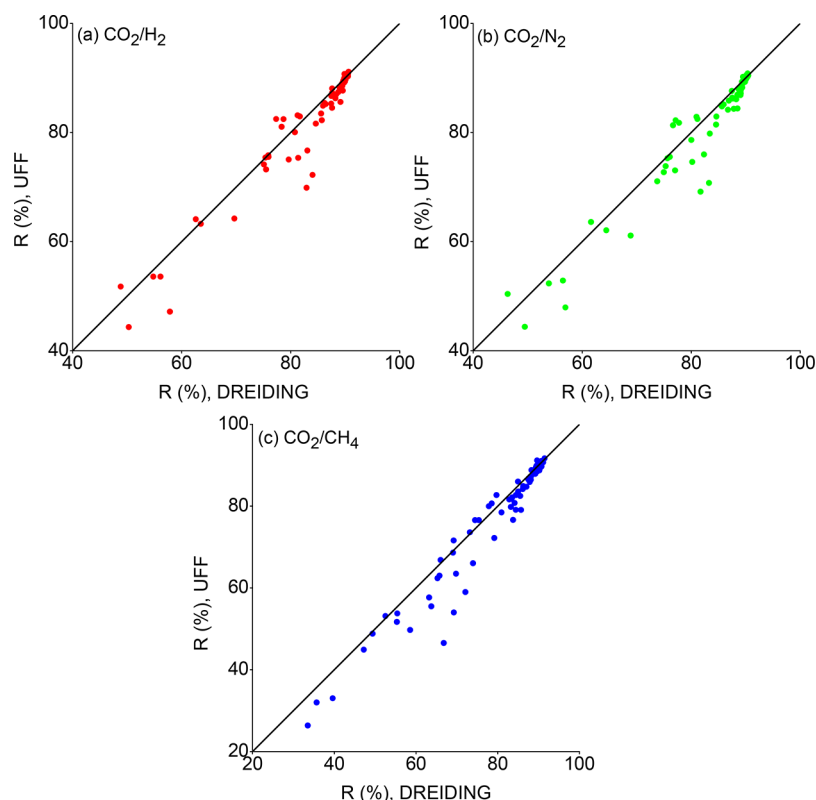


Figure 5. Comparison of percent regenerabilities of MOFs computed using Dreiding and UFF for (a) CO_2/H_2 , (b) CO_2/N_2 , and (c) CO_2/CH_4 mixtures. Diagonal lines are to guide the eye.

material lists of Dreiding and UFF. Ranking of the materials is very similar. For example, EMIVAY, EYOQAL, and BERGAI01 are identified as the top three selective MOFs based on the Dreiding. EYOQAL is the first, EMIVAY is the second, and BERGAI01 is the third MOF in the selectivity ranking of UFF-based simulations. Similarly, 8 MOFs are common in the promising material list for CO_2/N_2 separation. Ranking of the first 4 MOFs is very similar in both lists. For instance, KEYFIF01 and KEYFIF are the first and the second materials in both rankings. The third and fourth MOFs, EMIVAY and EYOQAL, identified based on the Dreiding only change their places as the fourth and third in the UFF-based list. All MOFs except one are the same in CO_2/CH_4 selectivity rankings. Rankings of top 5 MOFs for CO_2/CH_4 selectivity are very similar. For instance, KEYFIF has the second highest selectivity in both lists. The first and the third MOFs according to Dreiding results are KEYFIF01 and GIWNUV, and they are the third and first MOF, respectively, in the UFF-based list. The numbers of identical MOFs in top 10 rankings based on molecular simulations employing different FFs are also tabulated in Table S2. The high number of common MOFs that appear in both lists indicate that Dreiding and UFF predict similar selectivity ranking of MOFs, supporting the further use of these two generic FFs in high-throughput screening studies to identify the most selective adsorbents for CO_2 separations.

The most promising 10 MOFs based on the CO_2 working capacities are also given in Table 4. There are 6, 6, and 8 common MOFs in the Dreiding and UFF lists for CO_2/H_2 , CO_2/N_2 , and CO_2/CH_4 separations, respectively. Rankings of the top 3 MOFs are very similar for CO_2/H_2 , and the top 2 MOFs are the same for CO_2/N_2 . Although 8 MOFs are common in the list, their rankings are quite different for $\text{CO}_2/$

CH_4 separation. For example, the tenth MOF in the list of Dreiding is the first MOF in the UFF list. This result supports the lowest R^2 value between the predicted performance metrics of Dreiding and UFF for the CO_2 working capacity of CO_2/CH_4 mixture as shown in Table 3. There are 8, 7, and 7 common MOFs in the Dreiding and UFF lists for S_{sp} rankings of MOFs for CO_2/H_2 , CO_2/N_2 , and CO_2/CH_4 separations, respectively. The first two MOFs for CO_2/H_2 mixture and top 5 (4) MOFs for CO_2/N_2 (CO_2/CH_4) mixture are the same in both lists. Here, it is important to note that although the S_{sp} rankings have many common MOFs, there are significant quantitative differences in S_{sp} values of the top promising MOFs identified by Dreiding and UFF. Seven out of the top 10 MOFs for regenerability ranking are identical for CO_2/H_2 separation. The top 3 MOFs identified in the Dreiding-based simulations rank as first, fifth, and tenth in the UFF-based list. Although 8 of the top 10 MOFs are common in both lists for CO_2/N_2 separation, their rankings are different. For example, the top 4 MOFs in the Dreiding-based list are fifth, seventh, second, and first in the list of UFF. Finally, there are 8 identical MOFs in the regenerability lists for CO_2/CH_4 separations. The first, sixth, eighth, and tenth of the top 10 MOFs in the Dreiding list have the same rankings with the UFF list. Since these top MOFs have not been experimentally tested for CO_2 separations to the best of our knowledge, we are not able to make a comparison between experimentally measured and simulated performance evaluation metrics. The good agreement between experimentally measured and predicted CO_2/H_2 , CO_2/N_2 , and CO_2/CH_4 selectivities of various MOFs was shown in Figure S1, and we believe that our computational approach will make accurate estimates for the selectivities of MOFs which have not been experimentally tested yet.

Table 4. Top 10 MOFs for CO₂/H₂, CO₂/N₂, and CO₂/CH₄ Separations Based on the Performance Evaluation Metrics Computed Using Dreiding or UFF in the Molecular Simulations

		Dreiding			UFF										
S	ΔN (mol/kg)	S _{sp}	R (%)	S	ΔN (mol/kg)	S _{sp}	R (%)								
CO ₂ /H ₂															
EMVAY	2237.35	EMHAK	2.22	EYOQAL	399712.29	GALBUS	90.64	EYOQAL	3119.09	HAKJOU	2.34	EYOQAL	689817.90	GALBUS	91.12
EYOQAL	2074.29	HAKJOU	1.94	EMVAY	320862.42	IDIWOH	90.53	EMVAY	2657.41	EMHAK	2.11	EMVAY	396894.35	DIDBID	90.89
BERGAI01	1692.67	EYOPOY	1.78	BERGAI01	204453.75	LECEQEQ	90.52	BERGAI01	1977.81	EYOPOY	2.10	OCIZIL	275032.38	DIDBOJ	90.81
EYOPOE	1185.13	AJIHOQ	1.66	EMHAK	153268.06	DIDBID	90.45	BOWSIQ	1574.21	ACODED	2.01	BERGAI01	267405.19	EMHAK	90.72
KEYFIF01	1145.27	EYOQAL	1.65	KEYFIF01	124385.74	WOBHIF	90.38	EYOPOE	1526.30	HAKJOU	1.98	BOWSIQ	247581.23	IDIWOH	90.65
QJFLOI	1115.11	RAYLIO	1.57	KEYFIF	115796.15	DIDBOJ	90.34	LUXDEO	1492.43	AJIHOQ	1.93	HAKJOU	239714.86	HASSUR	90.47
KEYFIF	1102.57	HAKJOU	1.50	HAKJOU	113261.26	LARVIL	90.32	OCIZIL	1371.82	DEJROB	1.89	QJFLOI	200871.41	LARVIL	90.42
BOWSIQ	979.93	EMVAY	1.47	QJFLOI	104208.24	KUGZIW	90.32	QJFLOI	1354.35	LUXDEO	1.86	LUXDEO	190800.84	KUGZIW	90.36
PEQHOK	808.73	NUTQEZ	1.42	BOWSIQ	87513.61	OWIVIEW	90.29	KEYFIF01	1272.47	NEFTOJ	1.83	EBEMOO	163889.32	LUKLIN	90.31
HAKJOU	769.15	RAYLOU	1.42	OCIZIL	86404.58	HECQUB	90.27	KEYFIF	1237.20	RAYLIO	1.76	KEYFIF01	153588.38	LECEQEQ	90.31
CO ₂ /N ₂															
KEYFIF01	202.30	EMHAK	2.12	KEYFIF01	5178.36	IDIWOH	90.47	KEYFIF01	197.48	HAKJOU	2.19	EYOQAL	8980.72	LECEQEQ	90.83
KEYFIF	196.58	HAKJOU	1.77	KEYFIF	4875.75	LARVIL	90.44	KEYFIF	192.48	EMHAK	1.98	KEYFIF01	4538.97	GALBUS	90.71
EMVAY	119.89	RAYLIO	1.58	EYOQAL	2364.93	GALBUS	90.42	EYOQAL	183.24	AJIHOQ	1.83	KEYFIF	4415.73	DIDBID	90.62
EYOQAL	114.87	EYOQAL	1.57	EMVAY	1410.22	LECEQEQ	90.38	EMVAY	140.05	ACODED	1.82	EMVAY	2375.10	WOBHIF	90.50
RAYLIO	88.62	AJIHOQ	1.56	BERGAI01	1065.31	OWIVIEW	90.31	BERGAI01	123.01	HAKJOU	1.81	BERGAI01	2276.71	IDIWOH	90.48
BERGAI01	88.05	EYOPOY	1.47	EMHAK	933.91	DIDBOJ	90.30	EYOPOE	105.87	EYOPOY	1.79	LUXDEO	1634.31	DIDBOJ	90.43
EYOPOE	83.33	EMVAY	1.38	RAYLIO	863.30	DIDBID	90.27	LUXDEO	98.70	DEJROB	1.78	OCIZIL	1265.47	LARVIL	90.40
QJFLOI	75.48	RAYLOU	1.36	QJFLOI	802.52	KUGZIW	90.24	BOWSIQ	92.95	NEFTOJ	1.75	HAKJOU	1247.89	KUGZIW	90.25
YOZBOF	73.58	NUTQEZ	1.36	EBEMOO	682.03	LUKLIN	90.22	RAYLIO	84.30	RAYLIO	1.72	QJFLOI	1120.95	HECQUB	90.23
BOWSIQ	73.17	HAKJOU	1.34	NUJCIE	656.31	OWITAQ	90.22	EBEMOO	80.76	LUXDEO	1.71	EBEMOO	1118.21	LUKLIN	90.21
CO ₂ /CH ₄															
KEYFIF01	59.38	LECEQEQ	3.81	KEYFIF01	2276.69	IDIWOH	91.48	GIWNUV	60.97	DIDBID	4.03	EYOQAL	10698.50	IDIWOH	91.68
KEYFIF	55.29	AJIHOQ	3.63	KEYFIF	1919.38	OWIVIEW	91.12	KEYFIF	51.86	NUTQEZ	4.02	GIWNUV	1622.66	LARVIL	91.17
GIWNUV	47.61	NUTQEZ	3.63	GIWNUV	1247.37	KUGZIW	90.78	KEYFIF01	51.82	GALBUS	3.98	KEYFIF	1619.34	HECQUB	91.03
EYOPOE	22.29	FIQCEN	3.47	EYOQAL	509.95	WOBHIF	90.74	EYOQAL	30.22	AJIHOQ	3.80	KEYFIF01	1609.06	LUKLIN	90.73
EYOQAL	18.71	EMHAK	3.43	EMHAK	503.76	OWITAQ	90.73	EYOPOE	27.33	NEFTOJ	3.77	EYOPOE	987.38	OWIVIEW	90.69
LARVIL	18.52	HASSUR	3.39	LARVIL	389.94	OWIVAS	90.72	RAYLIO	18.74	HASSUR	3.70	EMHAK	600.43	OWIVAS	90.65
RAYLIO	18.39	NEFTOJ	3.17	EYOPOE	365.12	HECQUB	90.69	EMHAK	16.72	EMHAK	3.68	HAKJOU	510.59	OWITAQ	90.64
NUJCIE	16.93	EMHIS	2.74	AJIHOQ	284.63	OWITOE	90.61	NUJCIE	16.69	LECEQEQ	3.54	LUXDEO	462.51	OWITOE	90.59
EMHAK	16.23	GALBUS	2.53	LECEQEQ	252.81	LUKLIN	90.61	BOWSIQ	16.43	WOBHIF	3.40	AJIHOQ	371.08	OWITUK	90.58
EMVAY	16.14	DIDBID	2.50	NUJCIE	232.24	OWITEU	90.57	EMVAY	15.88	DIDBOJ	3.39	BOWSIQ	348.77	OWITEU	90.55

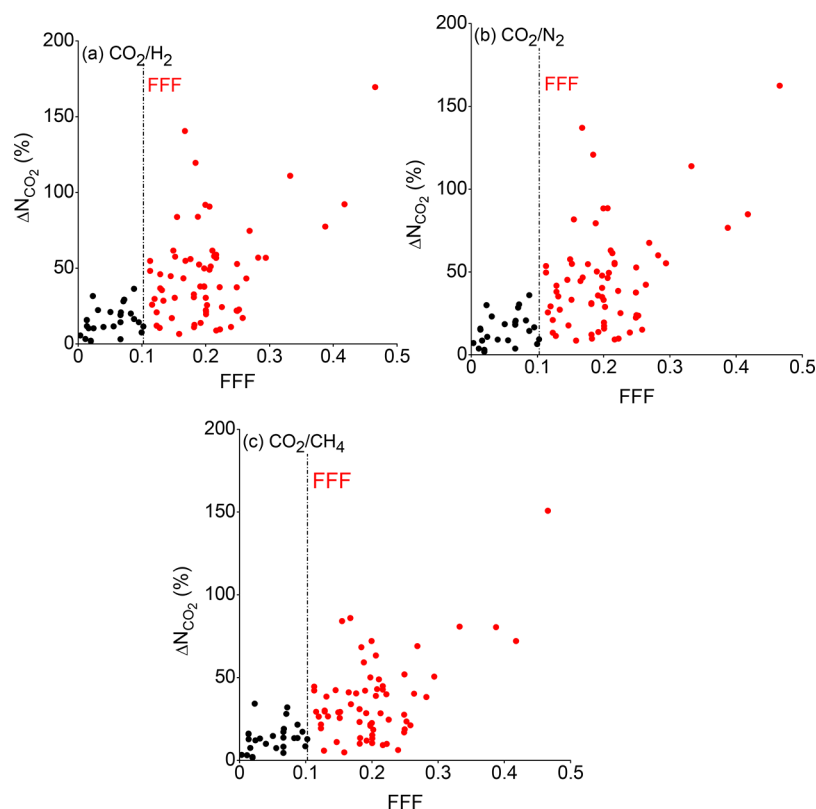


Figure 6. Relation between change in the CO₂ uptake and FFF for (a) CO₂/H₂, (b) CO₂/N₂, and (c) CO₂/CH₄ mixtures. The vertical dashed lines are given to differentiate between the MOFs that are sensitive to the FF type (on the right) and the ones that are not sensitive to the FF type (on the left).

In order to quantify the robustness of the ranking of MOFs to the FF selection, we also computed the Spearman's ranking correlation coefficients (SRCC). Values of SRCC change from -1 to 1 and indicate the correlation between two sets of ranking lists. Table S3 shows that SRCC is 0.98, 0.95, 0.97, and 0.96 for S , ΔN , S_{sp} , and $R\%$, respectively. This analysis suggests that the rankings of 100 MOFs based on the Dreiding FF are positively correlated with those based on the UFF, and strength of the correlation is very high. These results show that either of the generic FF can be safely used to screen and rank MOFs based on the four adsorbent performance evaluation metrics that we considered in this work. Throughout the manuscript, our aim is not to show superiority/accuracy of one generic FF over another but to understand how the ranking of the best MOF adsorbents changes based on the FF type. Results show that adsorbent evaluation metrics quantitatively change due to the differences in the predicted CO₂ uptakes of MOFs depending on the FF. In order to provide a guideline for the simulators in selecting either Dreiding or UFF, we proposed a simple factor that assesses sensitivity of the CO₂ uptake to the FF type. With this factor, we aim to differentiate between the MOFs for which using either Dreiding or UFF does not make any significant difference in the predicted CO₂ uptakes and the MOFs for which the type of the FF plays an important role in predicting the CO₂ uptakes and separation performance of the materials. The force field factor (FFF) was defined using the energy parameters of atoms in the Dreiding and UFF. Almost all atoms have different energy and size parameters (ϵ/k_B and σ , respectively) in each FF. For example, carbon is available in all MOFs, its ϵ and σ parameters are 47.89 K and 3.47 Å in Dreiding, whereas 52.87 K and 3.43 Å, respectively in the UFF.

The FFF that we propose consists of energy parameters since adsorption mainly depends on the energetic interactions, the type and the number of atoms of the MOFs:

$$\text{FFF} = \frac{\left| \sum_i^N n_i \times \frac{n_i}{N} \times \epsilon_{i,\text{Dreiding}}/k_B - \sum_i^N n_i \times \frac{n_i}{N} \times \epsilon_{i,\text{UFF}}/k_B \right|}{\sum_i^N n_i \times \frac{n_i}{N} \times \epsilon_{i,\text{Dreiding}}/k_B} \quad (1)$$

Here, n_i is the number of atoms i , N is the total number of atoms of MOF, and ϵ_i/k_B is the energy parameter of the atom i . This term expresses how much the potential parameter changes when the UFF was used instead of the Dreiding. We examined the relation between the FFF and the changes in the predicted CO₂ uptakes of MOFs. The latter was defined as follows where the CO₂ uptake predicted by the Dreiding was taken as the reference:

$$\Delta N_{\text{CO}_2} \% = |N_{\text{CO}_2,\text{Dreiding}} - N_{\text{CO}_2,\text{UFF}}| / N_{\text{CO}_2,\text{Dreiding}} \times 100 \quad (2)$$

Figure 6 shows $\Delta N_{\text{CO}_2} \%$ as a function of the FFF for the MOFs. Black points in each figure represent the MOFs for which the predicted CO₂ uptakes by two different FF vary less than 35%. In fact, 24 MOFs have less than 25% change in their CO₂ uptakes for CO₂/H₂, CO₂/N₂, and CO₂/CH₄ mixtures. The FFF of MOFs shown with black points in Figure 6 are less than 0.1, and their average FFF is 0.05. These are the MOFs that are not sensitive to the FF type. In other words, the area at the left of the vertical dashed lines shown in Figure 6 shows the safe zone to the simulators, where predictions for the CO₂

uptake of MOFs would not significantly change depending on the FF used in molecular simulations. For example, EMIHAK has the lowest FFF, 0.003. Due to its low FFF, the $\Delta N_{\text{CO}_2}\%$ values for this MOF are low: 5, 7 and 3% for CO_2/H_2 , CO_2/N_2 , and CO_2/CH_4 mixtures, respectively. The CO_2/H_2 , CO_2/N_2 , and CO_2/CH_4 selectivities of EMIHAK predicted from Dreiding are 704.52, 55.12, and 16.23, respectively, and these are very similar to the ones predicted by UFF, 636.46, 50.15, and 16.72. On the basis of the working capacity rankings, EMIHAK is the first MOF in the Dreiding list and second MOF in the UFF list for CO_2/H_2 and CO_2/N_2 mixtures and is the fifth MOF in the Dreiding list and seventh MOF in the UFF list for CO_2/CH_4 . This result shows that ranking of the MOFs having low FFF is not significantly affected from the FF.

Figure 6 shows that if the FFF is computed to be higher than 0.1, then Dreiding and UFF are expected to make different predictions for the CO_2 uptakes of MOFs, which also means that ranking of MOF adsorbents for CO_2 separations may be different. Red points in Figure 6 represent the MOFs for which the two FFs make different estimates for the CO_2 uptake. Most MOFs have more than 40% change in the CO_2 uptakes and their average FFF is 0.203. For example, LUXDEO has a high FFF, 0.42 leading to very high $\Delta N_{\text{CO}_2}\%$ values of 92, 85, and 72% for CO_2/H_2 , CO_2/N_2 , and CO_2/CH_4 mixtures, respectively. As a result, its performance evaluation metrics significantly change depending on the FF. For example, CO_2/H_2 selectivity of LUXDEO was predicted to be 695 by the Dreiding and 1492 by the UFF. LUXDEO was in the highly selective MOF lists determined by the UFF but it did not appear in the Dreiding list. At that point, it is important to note that not all the MOFs having $\text{FFF} > 0.1$ have high $\Delta N_{\text{CO}_2}\%$ as can be seen from Figure 6. There are several MOFs with FFF of 0.1–0.25, and half of them have low $\Delta N_{\text{CO}_2}\%$. However, MOFs with $\text{FFFs} > 0.3$ are the ones that show the highest deviations between Dreiding and UFF predictions for the CO_2 uptake. Therefore, it is better to use the FFF to quantitatively define the safe region: If the FFF is less than 0.1, then either the Dreiding or the UFF can be used to evaluate the CO_2 uptake and adsorption-based CO_2 separation potential of MOFs.

It is also a good practice to examine why low (high) FFF leads to small (large) changes in the CO_2 uptakes. We defined the FFF to show the change in the potential parameters of atoms. For example, OWITIY has the second lowest FFF, 0.01. This MOF has Mn, and since its energy parameter is not available in Dreiding, it was taken from the UFF. Therefore, there is no difference for the ϵ/k_B of metal atoms. The energy parameters of 144 C and 52 H atoms increased from 47.88 to 52.87 K and 7.65 to 22.15 K, respectively, when the UFF was used instead of the Dreiding. However, this increase was balanced by the decrease in the energy parameters of 96 O atoms from 48.19 to 30.21 K. As a result, the FFF is small for that MOF. In other words, the increase in the energy parameters of (C + H) is balanced with the decrease in energy parameters of (N + O) for the MOFs having low FFFs. In contrast, MOFs with high FFFs are either those having a metal atom which shows a large change when the FF is switched from Dreiding to UFF (such as OFERUN) or those having a large number of C and H atoms in their structures (such as GUPCOK). In the case of OFERUN, the energy parameter of Zn significantly increases when the UFF was used and leads to a high FFF of 0.39. GUPCOK has large number of C and H atoms, and the UFF part of the eq 1 dominates the Dreiding

part and leads to a large FFF of 0.46 for that MOF. Supporting this argument, the average of ratio of sum of C and H atoms to the total number of atoms in MOFs is 0.76 for the MOFs having high FFF whereas it is 0.62 for the MOFs having low FFFs. Atoms type and numbers of the MOFs having the five lowest and highest FFFs are also given in Table S4.

Finally, it is important to note that we aim to arbitrarily define a simple parameter that can be very quickly calculated before the molecular simulations to make a decision of using either Dreiding or UFF. Several other factors which affect the adsorption strength of the gases in the MOFs such as topology of the material, pore size, and pore shape have not been considered in the definition of FFF. The usefulness of the FFF is the following: Before computationally demanding simulations, one can calculate the FFF within seconds only considering the number and type of the atoms present in the MOF. If this value is smaller than 0.1, then either of the generic FFs can be used, since they will give similar estimates for CO_2 uptakes of MOFs and hence similar rankings of the MOF adsorbents. However, we would like to reiterate that having a low FFF does not mean that either Dreiding or UFF are necessarily accurate for this MOF, it just means that they are interchangeable. There may be cases that the best thing to do would be to use neither and develop a new model. If the FFF is higher than 0.1, significant quantitative differences can be expected for the CO_2 predictions of the Dreiding and UFF. In this case, obtaining experimental data to validate the selection of the FF or performing more detailed quantum-level calculations can be considered since the MOF is sensitive to the FF type.

4. CONCLUSION

This study examined the impact of the FF selection on high-throughput computational screening of MOFs for CO_2/H_2 , CO_2/N_2 , and CO_2/CH_4 separations. We performed molecular simulations for 100 MOFs using Dreiding and repeated these simulations using UFF to compute adsorption of CO_2/H_2 , CO_2/N_2 , and CO_2/CH_4 mixtures. Four adsorbent evaluation metrics, selectivity, working capacity, sorbent selection parameter, and regenerability were calculated using the results of Dreiding and UFF-based simulations and they were compared. Results showed that while there are quantitative differences in the computed metrics, ranking of MOFs is similar for two different FFs, especially in terms of selectivity and regenerability, which are the key parameters to select the most promising materials. Therefore, it is concluded that both FFs can be used in high-throughput molecular simulations of MOFs to identify the useful materials for adsorption-based CO_2 separations. We also defined a FFF and showed its relation with the change in CO_2 uptakes of MOFs to guide the simulators. If the FFF value of a MOF is lower than 0.1, then the role of the FF on the CO_2 uptake predictions is negligible; however, if the FFF is higher than 0.3, then significant quantitative differences in the predicted CO_2 uptakes, adsorbent evaluation metrics, and MOF rankings can be observed. With this FFF, the safe region in which the results of molecular simulation do not significantly change depending on the type of generic FF is shown. These results will be of great interest for researchers working on molecular simulations of MOFs by providing insights into choosing the appropriate FF.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.7b04792.

Potential parameters of the MOF atoms in UFF and Dreiding; number of common MOFs in top 10 material rankings based on molecular simulations performed using Dreiding and UFF; Spearman's ranking correlation coefficient (SRCC) between Dreiding-based and UFF-based rankings of 100 MOFs; five MOFs with the highest and lowest FFFs, comparison of simulation results with the experiments for CO₂/H₂, CO₂/N₂, and CO₂/CH₄ selectivities of various MOFs; comparison of gas uptakes and CO₂/H₂, CO₂/N₂, and CO₂/CH₄ selectivities of MOFs calculated with Dreiding and UFF (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: skeskin@ku.edu.tr.

ORCID

Seda Keskin: 0000-0001-5968-0336

Notes

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■ REFERENCES

- (1) Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. The Chemistry and Applications of Metal-Organic Frameworks. *Science* **2013**, *341* (6149), 974–986.
- (2) Meek, S. T.; Greathouse, J. A.; Allendorf, M. D. Metal-Organic Frameworks: A Rapidly Growing Class of Versatile Nanoporous Materials. *Adv. Mater. (Weinheim, Ger.)* **2011**, *23* (2), 249–267.
- (3) Qiu, S.; Xue, M.; Zhu, G. Metal-Organic Framework Membranes: From Synthesis to Separation Application. *Chem. Soc. Rev.* **2014**, *43* (16), 6116–6140.
- (4) Liu, Y.; Wang, Z. U.; Zhou, H. C. Recent Advances in Carbon Dioxide Capture with Metal-Organic Frameworks. *Greenhouse Gases: Sci. Technol.* **2012**, *2* (4), 239–259.
- (5) Belmabkhout, Y.; Guillerm, V.; Eddaoudi, M. Low Concentration CO₂ Capture Using Physical Adsorbents: Are Metal–Organic Frameworks Becoming the New Benchmark Materials? *Chem. Eng. J. (Amsterdam, Neth.)* **2016**, *296*, 386–397.
- (6) Keskin, S.; van Heest, T. M.; Sholl, D. S. Can Metal-Organic Framework Materials Play a Useful Role in Large-Scale Carbon Dioxide Separations? *ChemSusChem* **2010**, *3* (8), 879–891.
- (7) Li, J.-R.; Ma, Y.; McCarthy, M. C.; Sculley, J.; Yu, J.; Jeong, H.-K.; Balbuena, P. B.; Zhou, H.-C. Carbon Dioxide Capture-Related Gas Adsorption and Separation in Metal-Organic Frameworks. *Coord. Chem. Rev.* **2011**, *255* (15), 1791–1823.
- (8) Lu, X.; Jin, D.; Wei, S.; Wang, Z.; An, C.; Guo, W. Strategies to Enhance CO₂ Capture and Separation Based on Engineering Absorbent Materials. *J. Mater. Chem. A* **2015**, *3* (23), 12118–12132.
- (9) Ben-Mansour, R.; Habib, M.; Bamidele, O.; Basha, M.; Qasem, N.; Peedikakkal, A.; Laoui, T.; Ali, M. Carbon Capture by Physical Adsorption: Materials, Experimental Investigations and Numerical Modeling and Simulations—a Review. *Appl. Energy* **2016**, *161*, 225–255.

(10) Colon, Y. J.; Snurr, R. Q. High-Throughput Computational Screening of Metal-Organic Frameworks. *Chem. Soc. Rev.* **2014**, *43* (16), 5735–5749.

(11) Jiang, J. W.; Babarao, R.; Hu, Z. Q. Molecular Simulations for Energy, Environmental and Pharmaceutical Applications of Nanoporous Materials: From Zeolites, Metal-Organic Frameworks to Protein Crystals. *Chem. Soc. Rev.* **2011**, *40* (7), 3599–3612.

(12) Bao, Y.; Martin, R. L.; Simon, C. M.; Haranczyk, M.; Smit, B.; Deem, M. W. In Silico Discovery of High Deliverable Capacity Metal Organic Frameworks. *J. Phys. Chem. C* **2015**, *119* (1), 186–195.

(13) Thornton, A. W.; Simon, C. M.; Kim, J.; Kwon, O.; Deeg, K. S.; Konstas, K.; Pas, S. J.; Hill, M. R.; Winkler, D. A.; Haranczyk, M.; Smit, B. Materials Genome in Action: Identifying the Performance Limits of Physical Hydrogen Storage. *Chem. Mater.* **2017**, *29* (7), 2844–2854.

(14) Bordiga, S.; Vitillo, J. G.; Ricchiardi, G.; Regli, L.; Cocina, D.; Zecchina, A.; Arstad, B.; Bjørgen, M.; Hafizovic, J.; Lillerud, K. P. Interaction of Hydrogen with MOF-5. *J. Phys. Chem. B* **2005**, *109*, 18237–18242.

(15) Sagara, T.; Klassen, J.; Ganz, E. Computational Study of Hydrogen Binding by Metal-Organic Framework-5. *J. Chem. Phys.* **2004**, *121* (24), 12543–12547.

(16) Yang, Q.; Zhong, C. Molecular Simulation of Adsorption and Diffusion of Hydrogen in Metal-Organic Frameworks. *J. Phys. Chem. B* **2005**, *109* (24), 11862–11864.

(17) Yang, Q.; Zhong, C. Understanding Hydrogen Adsorption in Metal-Organic Frameworks with Open Metal Sites: A Computational Study. *J. Phys. Chem. B* **2006**, *110* (2), 655–658.

(18) Rappe, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A.; Skiff, W. M. UFF, a Full Periodic Table Force Field for Molecular Mechanics and Molecular Dynamics Simulations. *J. Am. Chem. Soc.* **1992**, *114*, 10024.

(19) Mayo, S. L.; Olafson, B. D.; Goddard, W. A. Dreiding: A Generic Force Field for Molecular Simulations. *J. Phys. Chem.* **1990**, *94* (26), 8897–8909.

(20) McDaniel, J. G.; Li, S.; Tylianakis, E.; Snurr, R. Q.; Schmidt, J. R. Evaluation of Force Field Performance for High-Throughput Screening of Gas Uptake in Metal-Organic Frameworks. *J. Phys. Chem. C* **2015**, *119* (6), 3143–3152.

(21) Dzubak, A. L.; Lin, L. C.; Kim, J.; Swisher, J. A.; Poloni, R.; Maximoff, S. N.; Smit, B.; Gagliardi, L. Ab Initio Carbon Capture in Open-Site Metal-Organic Frameworks. *Nat. Chem.* **2012**, *4* (10), 810–816.

(22) Boyd, P. G.; Moosavi, S. M.; Witman, M.; Smit, B. Force-Field Prediction of Materials Properties in Metal-Organic Frameworks. *J. Phys. Chem. Lett.* **2017**, *8* (2), 357–363.

(23) Watanabe, T.; Sholl, D. S. Accelerating Applications of Metal–Organic Frameworks for Gas Adsorption and Separation by Computational Screening of Materials. *Langmuir* **2012**, *28* (40), 14114–14128.

(24) Wu, D.; Yang, Q.; Zhong, C.; Liu, D.; Huang, H.; Zhang, W.; Maurin, G. Revealing the Structure–Property Relationships of Metal–Organic Frameworks for CO₂ Capture from Flue Gas. *Langmuir* **2012**, *28* (33), 12094–12099.

(25) Qiao, Z.; Zhang, K.; Jiang, J. In Silico Screening of 4764 Computation-Ready, Experimental Metal–Organic Frameworks for CO₂ Separation. *J. Mater. Chem. A* **2016**, *4*, 2105–2114.

(26) Sumer, Z.; Keskin, S. Ranking of MOF Adsorbents for CO₂ Separations: A Molecular Simulation Study. *Ind. Eng. Chem. Res.* **2016**, *55* (39), 10404–10419.

(27) Keskin, S.; Liu, J.; Rankin, R. B.; Johnson, J. K.; Sholl, D. S. Progress, Opportunities, and Challenges for Applying Atomically Detailed Modeling to Molecular Adsorption and Transport in Metal-Organic Framework Materials. *Ind. Eng. Chem. Res.* **2009**, *48* (5), 2355–2371.

(28) Allen, F. H. The Cambridge Structural Database: A Quarter of a Million Crystal Structures and Rising. *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *58* (3), 380–388.

(29) Frenkel, D.; Smit, B. *Understanding Molecular Simulation: From Algorithms to Applications*, 2nd ed.; Academic Press: San Diego, CA, 2002.

(30) Greathouse, J. A.; Allendorf, M. D. Force Field Validation for Molecular Dynamics Simulations of IRMOF-1 and Other Isoreticular Zinc Carboxylate Coordination Polymers. *J. Phys. Chem. C* **2008**, *112* (15), 5795–5802.

(31) Haldoupis, E.; Watanabe, T.; Nair, S.; Sholl, D. S. Quantifying Large Effects of Framework Flexibility on Diffusion in MOFs: CH₄ and CO₂ in ZIF-8. *ChemPhysChem* **2012**, *13* (15), 3449–3452.

(32) Pérez-Pellitero, J.; Amrouche, H.; Siperstein, F. R.; Pirngruber, G.; Nieto-Draghi, C.; Chaplais, G.; Simon-Masseron, A.; Bazer-Bachi, D.; Peralta, D.; Bats, N. Adsorption of CO₂, CH₄, and N₂ on Zeolitic Imidazolate Frameworks: Experiments and Simulations. *Chem. - Eur. J.* **2010**, *16* (5), 1560–1571.

(33) Sezginel, K. B.; Uzun, A.; Keskin, S. Multivariable Linear Models of Structural Parameters to Predict Methane Uptake in Metal-Organic Frameworks. *Chem. Eng. Sci.* **2015**, *124*, 125–134.

(34) Basdogan, Y.; Keskin, S. Simulation and Modelling of MOFs for Hydrogen Storage. *CrystEngComm* **2015**, *17* (2), 261–275.

(35) Potoff, J. J.; Siepmann, J. I. Vapor–Liquid Equilibria of Mixtures Containing Alkanes, Carbon Dioxide, and Nitrogen. *AIChE J.* **2001**, *47* (7), 1676–1682.

(36) Makrodimitris, K.; Papadopoulos, G. K.; Theodorou, D. N. Prediction of Permeation Properties of CO₂ and N₂ through Silicalite Via Molecular Simulations. *J. Phys. Chem. B* **2001**, *105* (4), 777–788.

(37) Buch, V. Path Integral Simulations of Mixed Para-D₂ and Ortho-D₂ Clusters: The Orientational Effects. *J. Chem. Phys.* **1994**, *100* (10), 7610–7629.

(38) Martin, M. G.; Siepmann, J. I. Transferable Potentials for Phase Equilibria. I. United-Atom Description of N-Alkanes. *J. Phys. Chem. B* **1998**, *102* (14), 2569–2577.

(39) Wilmer, C. E.; Kim, K. C.; Snurr, R. Q. An Extended Charge Equilibration Method. *J. Phys. Chem. Lett.* **2012**, *3* (17), 2506–2511.

(40) Li, W.; Rao, Z.; Chung, Y.; Li, S. The Role of Partial Atomic Charge Assignment Methods on the Computational Screening of Metal-Organic Frameworks for CO₂ Capture under Humid Conditions. *Chemistry Select* **2017**, *2* (29), 9458–9465.

(41) Bae, Y. S.; Snurr, R. Q. Development and Evaluation of Porous Materials for Carbon Dioxide Separation and Capture. *Angew. Chem., Int. Ed.* **2011**, *50* (49), 11586–11596.