Evaluation of Force Field Performance for High-Throughput Screening of Gas Uptake in Metal–Organic Frameworks

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Supporting Information

ABSTRACT: High-throughput computational screening is an increasingly useful approach to identify promising nanoporous materials for gas separation and adsorption applications. The reliability of the screening hinges on the accuracy of the underlying force fields, which is often difficult to access systematically. To probe the accuracy of common force fields and to assess the sensitivity of the screening results to this accuracy, we have computed CO₂ and CH₄ gas adsorption isotherms in 424 metal–organic frameworks using ab initio force fields and evaluated the contribution of electrostatic, van der Waals, and polarization interactions on the predicted gas uptake and the adsorption site probability distributions. While there are significant quantitative differences between gas uptake predicted by standard (generic) force fields (such as UFF) and ab initio force fields, the force fields predict similar ranking of the MOFs, supporting the further use of generic force fields in high-throughput screening studies. However, we also find that isotherm predictions of standard force fields may benefit from significant error cancellation resulting from overestimation of dispersion and neglect of polarization; as such, caution is warranted, as this error cancellation may vary among different classes of materials.

INTRODUCTION

Metal–organic frameworks (MOFs) have received a great deal of attention for applications including gas separation and storage, due primarily to their extremely high porosity and tunability. MOFs are synthesized through the self-assembly and crystallization of secondary-building units (SBUs), consisting of inorganic clusters acting as “nodes” connected by organic “linkers”, yielding millions of MOFs that could be potentially synthesized. Identifying and synthesizing promising candidate MOFs with tailored properties for specific application thus presents both a great opportunity and challenge.

High-throughput computational screening is becoming an increasingly popular tool to characterize large numbers of MOFs with respect to their gas adsorption and separation properties. Starting from ~30,000 experimentally documented metal–organic compounds in the Cambridge Structural Database, Watanabe and Sholl† identified 1163 structures as exhibiting a 3D network of connected atoms, and they computed CO₂ and N₂ gas adsorption and diffusion properties for a subset (359) that were deemed appropriately porous. Such efforts need not be restricted to materials that have been previously synthesized. Wilmer et al.‡ constructed a database of 137,953 hypothetical MOFs by exploiting the “building block” character of the constituent SBUs and screened these MOFs for their methane-storage capabilities. They identified hundreds of candidate MOFs with higher methane storage than any existing material at the time. Other high-throughput screening studies of gas adsorption in MOFs have targeted hydrogen uptake and deliverable capacity,³ CH₃/H₂ separation,⁴ and kinetically controlled gas separations.⁵ In some cases, the resulting data have been further synthesized to develop quantitative structure–property relationships (QSPR) that correlate gas adsorption properties with structural characteristics of the materials, providing both valuable insight and a basis for efficient prescreening of candidate structures.⁶–¹⁰ In addition, similar high-throughput screening studies have been conducted for gas adsorption/separation in zeolites.¹¹–¹⁵ For a comprehensive review of prior efforts regarding high-throughput screening of MOFs, we refer the interested reader to a recent review.¹⁶

All of these high-throughput screening applications rely on the ability to predict the gas-adsorption properties of MOFs with sufficient accuracy to yield meaningful results, while maintaining tractable computational efficiency. Grand canonical Monte Carlo (GCMC) simulations and variants, including hierarchically staged simulations,⁷ graphics processing unit
(GPU) implementations, and free energy grid-based lattice model simulations, allow for efficient computation of gas adsorption isotherms. However, the ability to accurately predict the gas adsorption of a given MOF structure is limited by the force field utilized to describe the adsorbate—framework and adsorbate—adsorbate interactions. (This assumes an accurately known or hypothetically realistic MOF structure—the validity of this assumption is an important but separate question that is beyond the scope of the present work.) In light of ongoing work in this area, it is vital to critically evaluate the ability of commonly employed force fields to predict gas adsorption properties of MOFs and the robustness of high-throughput screening applications with respect to force field accuracy.

In this work, we compute gas adsorption isotherms for CO2 and CH4 for a diverse set of 424 MOFs, comparing the predicted uptakes from “standard” force fields commonly used in high-throughput MOF screenings to those predicted from accurate ab initio force fields. The latter are based on symmetry-adapted perturbation theory (SAPT) and have been previously demonstrated to yield very accurate gas adsorption isotherms for a wide range of MOFs. To our knowledge, this is the largest set of MOFs for which first-principles-derived force fields, including explicit adsorbate polarization, have been used to calculate gas adsorption isotherms. Our primary goal is to examine the robustness of high-throughput screening predictions to different treatments of electrostatic, van der Waals (vdW), and polarization interactions between adsorbates and MOF frameworks. This analysis provides important insights regarding the reliability of common “generic” Lennard-Jones force fields in high-throughput screening for gas adsorption. In addition, our study provides a quantitative analysis of the underlying physical mechanisms dictating gas adsorption for a large database of MOFs, revealing general principles that are important for future studies of gas adsorption in MOFs.

**METHODS**

The hypothetical MOF structures were constructed based on previously reported methodologies. The structures encompass three different topologies, pcu, fcu, and ftf, and are built from two different inorganic clusters, namely Zn2O and Zr2O4(OH)4 and 20 organic linkers. The organic linkers are shown in Figure S1 (Supporting Information); they are ditopic (e.g., the commonly employed benzene dicarboxylate (BDC) linker) and tetrapolar linkers similar to those employed in ref 2 and in the recent MOF literature. The 10 ditopic linkers yield 10 pcu and 10 fcu structures, and the 10 tetrapolar linkers yield 10 ftf structures. Most of the MOFs were generated by functionalizing the original 30 “parent” MOFs with seven functional groups. The linkers were either singly or doubly functionalized with one of the following groups: Cl, Br, NH2, NO2, OH, COH (aldehyde), or COOH. The functionalization was completed in an automated way using the in-house software FunctionalizeThis. The obtained functionalized MOF structures were then optimized with constant cell size using the Forcite module in Materials Studio. To this set of 416 hypothetical MOFs, we added 8 experimentally known zeolitic imidazolate frameworks (ZIF-8, -25, -71, -68, -69, -78, -79, and -81) to increase structural diversity. It is important to note that none of the MOFs in this database contain coordinatively unsaturated metal sites, and thus there is no direct adsorbate—metal binding; modeling such systems may require specialized force fields or techniques and is beyond the scope of this work.

Isotherms for CO2 and CH4 were computed using our previously developed lattice-model based simulations. Briefly, a free energy grid with ~1 Å resolution is constructed for each MOF by averaging the Boltzmann factor over thousands of randomly sampled configurations of the particular adsorbate within a grid cell. This free energy grid provides a quantitative topological picture of the adsorption sites and exactly determines the gas uptake in the low-pressure limit and maintains high accuracy through the saturation pressure. At higher pressure, we introduce “coarse-grained” adsorbate—adsorbate interaction potentials and run lattice-based GCMS simulations, yielding dramatic speed-ups over conventional fully atomistic GCMS simulations. We employed Ewald sums (PME) to compute both electrostatic and vdW interactions out to infinite distance when generating the free energy grid. We note that only “pairwise” polarization effects are incorporated into the free energy grid, and true many-body polarization is not explicitly included; this should be a good approximation for computing CO2 and CH4 isotherms at low pressure. The resulting error in computed gas uptake of lattice-model simulations compared to fully atomistic GCMS simulations is negligible compared to the differences between force field predictions (see Figure S4 in Supporting Information). Simulation parameters of the lattice-model simulations are given in the Supporting Information.

The force fields that we employed can be classified into three types: (1) “standard” Lennard-Jones + Coulomb force fields describing adsorbate—MOF interactions; (2) SAPT-based, polarizable force fields describing adsorbate—MOF interactions; and (3) coarse-grained adsorbate—adsorbate potentials that are used in the lattice-model simulations. As prototypical examples of the “standard” force fields (and common choices in prior high-throughput screenings), we utilized the Lennard-Jones parameters from the universal force field (UFF) for the MOF framework and the popular EPM2 (CO2) and TraPPE (CH4) force fields for the adsorbate molecules. (Our general conclusions are not dependent on this specific choice; see Figures S4 and S5 in the Supporting Information.) The latter have been thoroughly benchmarked against neat fluid properties. The SAPT-based force fields (henceforth SAPT-FFs) have been previously described and we only briefly summarize here. These entirely ab initio force fields employ an explicit energy decomposition, with a one-to-one correspondence with the physically distinct intermolecular interaction energies of SAPT, namely electrostatics, exchange, induction, and dispersion. The exchange and other short-range interactions are treated with an exponential term, with damped Ce/Rn interaction terms (n = 6, 8, 10, 12) for dispersion, accounting for higher-order interactions. McDaniel et al. previously found that a highly accurate treatment of dispersion interactions is necessary for quantitatively predicting CO2 uptake in ZIFs. Explicit polarization is treated using Drude oscillators (for CO2). All parameters of SAPT-FF used in this work are given in the Supporting Information. The lattice GCMS simulations also require coarse-grained adsorbate—adsorbate potentials. For CO2, we employ the potential of Liu, while for CH4 we use the TraPPE force field.

It is widely recognized that an accurate description of electrostatic interactions is vital for predicting gas uptake (aside from nonpolar methane and noble gases). Correspondingly, there has been significant work to model these interactions.
using methods that are efficient enough for high-throughput screening. In this work, we obtain ab initio charges for each MOF using an efficient fragment approach. Making use of the “building block” nature of MOFs, we deconstruct the MOF into its inorganic and organic SBUs. These individual SBUs are then terminated with capping atoms, and DFT calculations followed by subsequent distributed multipole analysis (DMA) and charge fitting to the DMA are carried out for each unique capped SBU (these charges are henceforth termed “Q_{SBU}”). If the capping of these SBUs mimics the appropriate charge transfer between SBU units, then the derived atomic charges should be transferable to the bulk MOF, yielding an electrically neutral MOF. Validating this approach, we thus find only small net charge on each MOF (average absolute charge of 0.008 e/atom, with the maximally charged MOF exhibiting an absolute charge of 0.016 e/atom). We evenly “smear” a neutralizing charge among the constituent atoms to generate a neutral system. This charge fitting procedure is described in detail in the Supporting Information.

### RESULTS AND DISCUSSION

All CO2 uptakes reported in this paper have been computed at 298 K and 0.2 bar (representative of the partial pressure under flue gas conditions) and are given in absolute uptake (volume of gas at STP adsorbed per volume of MOF). Calculations at 1 bar are given in the Supporting Information (Figures S8–S12), with almost identical conclusions.

We use two different metrics to quantify the degree of correlation between predicted uptakes. In a high-throughput screening application, there may be a hierarchy of methods applied to analyze a database of MOFs. For example, a computationally inexpensive method with lower accuracy might be used as an initial prescreening, followed by a higher accuracy, more expensive method applied to a subset of the top performing materials as predicted by the inexpensive method. In the initial screening, it is therefore highly important to correctly rank the MOFs in order of performance, so that the subset of highest performing materials is correctly identified for further screening. We therefore calculate the Spearman rank correlation coefficient (SRCC) as a measure of the ability of a particular method to successfully rank the MOFs by performance (we report the square of this value, SRCC^2, for consistency with the reported Pearson correlation). The higher accuracy method, on the other hand, should make accurate quantitative predictions of the gas uptake of the MOFs, so that the top performing candidates can be compared with previously characterized, existing materials. We therefore perform a linear regression (constraining the intercept to zero) on the uptake data predicted by one method versus that predicted by another method. We report both the slope and R^2 values (square of the Pearson correlation coefficient) of this regression. All quantitative metrics are given in the corresponding figure captions. We note that all “lines” depicted in the figures in this paper correspond to the y = x line and serve to guide the eye; these lines do not represent the best-fit lines of the linear regression, and only the slope and R^2 values of the regression are given.

**Comparison of Electrostatic Treatments for Predicting CO2 adsorption in MOFs.** Accurate treatment of electrostatic interactions between adsorbates and MOFs is crucial for predicting CO2 uptake. Here we compare CO2 adsorption predicted by three different charge derivation schemes, in combination with the UFF/EPM2 force field. Note that even though the same force field is used to model vdW interactions in each case, the qualitative conclusions are somewhat dependent on the choice of force field because force fields determine the ratio of vdW to electrostatic interaction energies within the MOF. This ratio then determines the sensitivity of the computed uptake to the different charge-fitting schemes (see Supporting Information).

We first compare our Q_{SBU} charge fitting method to the REPEAT charge fitting method of Campana and co-workers (see also Chen et al.40). In REPEAT, charges are fit to the electrostatic potential (ESP) generated by plane-wave DFT calculated electron densities in periodic systems. While this method has previously been used as an accurate “benchmark” to compare with other charge fitting schemes for MOFs,35,39,41 it is probably too computationally expensive to be utilized in many high-throughput screening applications, especially for MOFs with large unit cells. In Figure 1, we compare the CO2 uptake for 24 MOFs as computed using REPEAT derived charges compared to Q_{SBU} charges. While the 24 MOFs were chosen for computational convenience based on their relatively small unit cells (less than ~20 Å^3), they encompass all functional groups studied, and their CO2 uptakes span the range present in the full set of 424 MOFs.

There is satisfactory agreement between uptakes predicted by the two different charge fitting methods. While there do exist quantitative differences (slope = 1.25), there is good correlation (SRCC^2 = 0.86, R^2 = 0.96) between the predictions from the two charge methods. Neither method should be considered a “benchmark”, as both methods have potential limitations: the Q_{SBU} charges are generated from cluster models, while the REPEAT method can lead to unphysical charges on buried atoms.41 However, the semiquantitative agreement between these methods gives confidence that the Q_{SBU} charge fitting scheme is robust and accurate enough for the purposes of this work. We note that we have employed this Q_{SBU} charge fitting scheme in previous works that have reproduced experimental adsorption isotherms in MOFs with excellent results.20,21,23

Methods for deriving charges for MOFs based on the charge equilibration (QE) method of Rappe and Goddard22 are a common choice in high-throughput screening due to their general applicability and computational efficiency.35–38 Here we examine the MOF electrostatic-potential-optimized charge scheme (MEPO-QEq) of Kadantsev et al.35 in which the QE
method is extended to periodic systems and specifically reparameterized for 543 MOFs based on fitting to \textit{ab initio} computed ESPs. All MEPO-QE parameters were taken from the work of Kadantsev et al., except for Zr where the original QE parameters were used (Zr was not refit in ref 35). We used an analogous periodic-QE algorithm to that described previously by Haldoupis et al.\footnote{34} Figure 2 compares the predicted CO$_2$ uptake using MEPO-QEq charges, no charges, and our $Q_{SBU}$ charges. The correlation coefficients as well as the slopes of the best fit line(s) are very similar to those reported in ref 35 (note we report the \textit{squares} of the correlation coefficients), although we have used a different “benchmark” charge method ($Q_{SBU}$). The uptakes predicted by the MEPO-QEq method are modestly but systematically underestimated. While the correlation coefficients are high for predicted uptakes using the MEPO-QEq method compared to our $Q_{SBU}$ method (SRCC$^2 = 0.94$, $R^2 = 0.96$), they are (quite surprisingly) also high for the analogous comparison \textit{without} any charges (SRCC$^2 = 0.90$, $R^2 = 0.94$). Note that the contribution of electrostatics is overall very significant, as computed uptakes are dramatically lower when computed without charges. Differences between these electrostatic treatments are further magnified if explicit polarization of gas molecules is taken into account (\textit{vide infra}). An analogous comparison between predicted CO$_2$ uptake for the same electrostatic treatments with the SAPT-FF force field for vdW interactions is given in the Supporting Information (Figures S6 and S7). Interestingly, in that case there is qualitatively worse agreement between gas-uptake predictions using MEPO-QEq charges and no charges as compared to $Q_{SBU}$ charges. The differences in the conclusions are due to systematic differences in the strength of vdW interactions between UFF and SAPT-FF.

All subsequent calculations employ our $Q_{SBU}$ charges for MOFs so as to isolate the importance of vdW and polarization interactions while using a consistent and accurate treatment of electrostatics.

**Figure 2.** CO$_2$ uptake computed using MEPO-QEq charges compared to that using $Q_{SBU}$ charges (red symbols): SRCC$^2 = 0.94$, $R^2 = 0.96$, slope = 0.84. CO$_2$ uptake computed using no charges compared to that using $Q_{SBU}$ charges (green symbols): SRCC$^2 = 0.90$, $R^2 = 0.94$, slope = 0.58. The black line is $y = x$ to guide the eye.

\textbf{Analysis of vdW and Polarization Force Field Components for Predicting CO$_2$ Adsorption in MOFs.} In conjunction with electrostatics, the force field chosen to describe adsorbate–MOF vdW interactions governs the predicted gas uptake. To the best of our knowledge, all previous high-throughput screening studies of gas adsorption in MOFs have employed standard, “generic,” Lennard-Jones-type force fields (e.g., UFF\footnote{28} or Drieding\footnote{43}) in combination with empirically fit adsorbate force fields (e.g., TraPPE\footnote{30,44} or EPM2).\footnote{29} Although there is some data benchmarking such force fields for screening purposes,\footnote{45} other works have shown substantial quantitative and sometimes even qualitative differences as compared to experiment, with particularly high discrepancies reported for ZIFs.\footnote{46–49} Furthermore, these standard force fields do not include explicit polarization, potentially leading to significant error when treating MOFs with strongly polar environments. As a benchmark, we compute gas uptake using our SAPT-FF force field to describe vdW interactions and explicitly incorporate CO$_2$ polarization.\footnote{31} With SAPT-FF, we have previously found semiquantitative to quantitative accuracy vs experimentally measured gas adsorption isotherms for a number of functionalized MOFs.\footnote{20–23} Since the force fields employ no empirical parameters, we anticipate similar accuracy for the present systems.

In Figure 3, we compare the predicted CO$_2$ uptake using the UFF/EPM2 force field to that computed using our SAPT-FF force field for the database of MOFs. There exists a relatively clear hierarchy among the MOF topologies, with pcu < ftw < fcu for low-pressure CO$_2$ uptake. This hierarchy seems to inversely correlate with the porosity of the MOFs within these topologies (\textit{vide infra}), with low-porosity MOFs generally exhibiting higher CO$_2$ uptake. Significant quantitative differences in the prediction of CO$_2$ uptake between the two force fields exist, at least for a significant subset of the MOFs. In particular, UFF/EPM2 significantly overpredicts CO$_2$ uptake as compared to SAPT-FF for ZIFs, consistent with prior observations.\footnote{25} However, there are other MOFs, mainly of the ftw and fcu topology, for which SAPT-FF predicts higher uptake than UFF/EPM2. Despite these discrepancies and the dramatic differences in the underlying force fields, there is overall good correlation (SRCC$^2 = 0.90$, $R^2 = 0.83$) between the force field predictions, with UFF/EPM2 generally predicting slightly lower uptake (slope = 0.91). We partially attribute the high SRCC value to the 2 orders of magnitude variation in CO$_2$ uptake across the different topologies (pcu, fcu, ftw); the SRCC values computed for MOFs within each topology are significantly lower. Nonetheless, the strong...
correlation suggests that generic force fields such as UFF may prove reliable for high-throughput screening predictions of low-pressure CO₂ uptake in MOFs (with no coordinatively unsaturated metal sites). However, the agreement between the predicted low-pressure gas uptakes at the UFF/EMP2 and SAPT-FF level obscures some crucial differences. As we will show below, this agreement is somewhat fortuitous, resulting from substantial cancellations in the differing treatments of short-range repulsion, long-range dispersion, and polarization between the force fields.

In Figure 4, we show a comparison of CO₂ uptakes computed with UFF/EMP2 compared to those computed with SAPT-FF without polarization (SAPT-FF-nopol) for the database of MOFs. This comparison isolates the differences in predicted uptake resulting from the different treatments of adsorbate−MOF vdW interactions. The slope of the best fit line (1.41) indicates that the UFF/EMP2 force field predicts systematically higher uptake than the SAPT-FF-nopol force field, resulting from the former’s generally stronger dispersion interaction energies between adsorbed CO₂ molecules and the MOF framework. This systematic trend has been previously noted and is a consequence of the different functional forms for the dispersion interactions employed by the different force fields; the Lennard-Jones force field has a single C₆/ᵣ⁶ term to model vdW interactions, while the SAPT-FF functional form employs an extended Cₙ/ᵣⁿ form (n = 6, 8, 10, 12) to account for higher-order dispersion interactions. To accurately predict the binding of the minimum energy complex, the C₆ term of the Lennard-Jones force field must be effectively ~30−40% larger to compensate for the neglect of higher-order terms, yielding dispersion interactions which are asymptotically too attractive. These small errors are magnified by the high density of atoms in the MOF crystal, resulting in systematic deviations in predictions of gas uptake.

We next seek to isolate the influence of adsorbate polarization. In Figure 5, we compare the CO₂ uptake as predicted by our SAPT-FF force field with (SAPT-FF) and without (SAPT-FF-nopol) polarization for the database of MOFs. As expected, we find that incorporation of adsorbate polarization yields substantially and systematically higher uptake (slope 0.65). However, while inclusion of polarization is essential for quantitatively accurate predictions, the high degree of correlation (SRCC² = 0.98, R² = 0.98) between the force field predictions indicates that it may not be necessary in order to correctly rank (or prescreen) a similar database of MOFs. This is a significant result, as the inclusion of polarization in a force field requires substantially greater computational expense (typically, between 2 and 10 times).

Even when force fields predict similar gas uptakes, they may do so for different reasons (e.g., dissimilar distribution of adsorbates, differing “physics” of adsorption). We therefore compare the different force fields in more detail. Our lattice-model based approach for computing adsorption isotherms naturally yields a free-energy grid of each MOF, corresponding to a probability distribution of adsorbing a gas molecule at a discrete volume (~1 Å³) within the MOF. This probability distribution contains much more information than the resulting adsorption isotherm, yielding a far more informative analysis of the different treatments of physical interactions between gas molecules and the MOF.

To characterize the (dis)similarity of these probability distributions, we compute the Bhattacharyya coefficient (BC) of the distributions, defined as

\[
BC(p, q) = \int \sqrt{p(r)q(r)} \, dr
\]

where p(r) and q(r) are the respective probability distributions for adsorbing a CO₂ molecule within the MOF (with ~1 Å³ resolution), as predicted by two different force fields. The BC coefficient is bounded by zero and one, with a value of one indicating perfect coincidence of the distributions.

Histograms of BC values derived from comparisons of different force fields are shown in Figure 6. The error cancellation resulting from the neglect of explicit polarization and overestimation of dispersion interactions, manifested in the computed CO₂ uptake for certain MOFs, does not appear in the adsorption site probability distributions. The adsorption site probability distributions are less similar as predicted by the UFF/EMP2 and SAPT-FF force fields that employ different treatments of both polarization and vdW interactions (average BC = 0.86) than the distributions predicted by the force fields that only deviate in the treatment of one of these interactions (average BC = 0.92). This indicates that the error cancellation that leads to reasonable quantitative agreement in predicted.

![Figure 4](image1.png)

**Figure 4.** CO₂ uptake computed using UFF/EMP2 compared to that using SAPT-FF-nopol. Hypothetical MOFs are grouped according to their topology; pcu = red symbols, fcu = green symbols, and ftw = blue symbols. Experimental ZIF structures are shown as purple symbols (black line is y = x to guide the eye). For the total set, SRCC² = 0.94, R² = 0.86, and slope = 1.41.

![Figure 5](image2.png)

**Figure 5.** CO₂ uptake computed using SAPT-FF-nopol compared to that using SAPT-FF. Hypothetical MOFs are grouped according to their topology; pcu = red symbols, fcu = green symbols, and ftw = blue symbols. Experimental ZIF structures are shown as purple symbols (black line is y = x to guide the eye). For the total set, SRCC² = 0.98, R² = 0.98, and slope = 0.65.
CO2 uptake by the UFF/EPM2 and SAPT-FF force fields is somewhat fortuitous. Thus, to the extent that these force fields differ primarily in their treatment of polarization and vdW interactions, the differing treatments of these physical interactions lead to different adsorption site distributions within each MOF.

We also illustrate the different effects of vdW and polarization interactions from another perspective. In Figure 7, we compare the energies of CO2 molecules adsorbed in the minimum-energy adsorption sites for each MOF, as computed using different force fields. In Figure 7b, it is clear that the inclusion of explicit polarization systematically shifts the adsorption energy to more negative values at these sites, with greater shifts occurring for stronger binding, electrostatically dominated adsorption sites. In contrast to this, the comparison of minimum adsorption site energies as predicted using different vdW interactions (UFF/EPM2 vs SAPT-FF-nopol (Figure 7a)) shows no such obvious systematic shift.

Taken together, these comparisons suggest that generic, nonpolarizable force fields of the Lennard-Jones + Coulomb form may benefit from significant error cancellation resulting from both the neglect of explicit polarization and the overestimation of asymptotic dispersion interactions. While such error cancellation has been commonly exploited in liquid-state simulation (as evidenced by the great success of many nonpolarizable, Lennard-Jones + Coulomb force fields for neat fluids), it is not a priori obvious that such error cancelation will be successful in MOFs due to their inhomogeneous and potentially highly polar nature. Thus, although our results suggest that generic force fields are likely sufficient for high-throughput prescreening of MOFs for gas adsorption, some caution is warranted.

Enhancement of CO2 Uptake by Incorporating Functional Groups in MOFs. It is widely recognized that functionalization of organic SBUs with polar groups can enhance low-pressure CO2 uptake in MOFs. We evaluated the performance of the seven functional groups present in our database of 424 MOFs, Cl, Br, NH2, OH, COOH, NO2, and COH (aldehyde), by computing the average percent enhancement in CO2 uptake for the respective functionalized MOFs compared to their unfunctionalized “parent” structures. We note that each MOF is functionalized with only one type of group, either adding one (single) or two (double) functional groups to each organic SBU in the MOF. We find that, on average, the percent enhancement is generally linear with the number of functional groups (see Figure S13 in Supporting Information). Deviations from linearity can be seen for carboxylic acid groups, where double functionalization typically leads to more than twice the enhancement of single functionalization. This “synergistic” effect results from the simultaneous interaction of a gas molecule with two or more functional groups (usually on different SBUs), with nonlinear enhancements in uptake caused by the exponential form of the Boltzmann factor, as a consequence of the combination of adsorbate size, MOF pore size and topology, and linker functionalization.23

It is interesting to examine how the predicted enhancement depends on the choice of force field. In Figure 8, we show the percentage enhancement (for the case of double functionalization) of each organic SBU as predicted by three of the previously described adsorbate-MOF force fields: (1) SAPT-FF in combination with Q_{SBU} charges; (2) UFF/EPM2 in combination with Q_{SBU} charges; (3) UFF/EPM2 in combination with MEPO-QE charges. From SAPT-FF/Q_{SBU}, we find that carboxylic acid functionalization enhances CO2 uptake the most, followed by relatively similar average enhancements from NH2, OH, NO2, and COH, and typically lower enhancements from halogen functionalization. It is important to note that while amine functionalization can lead to very high CO2 uptake enhancement through the formation of a carbamate species,51 all amine functionalization in our database of MOFs is “aniline-like”, such that the NH2 groups are adjacent to an aromatic...
ring; such systems do not form carbamates and interact only via physisorption. This predicted qualitative ordering of enhancement is largely retained with the UFF/EPM2/QSBU force field combination; however, there exist significant quantitative differences in the predicted percentage enhancement in many cases, and in general UFF/EPM2/QSBU predicts lower functional group enhancement than SAPT-FF/QSBU (due in part to neglect of polarization as well as differences in predicted uptake of the parent structure). The third force field combination, UFF/EPM2/MEPO-QEq, predicts a qualitatively different ordering compared to the other two force field combinations, implying that the prediction of functional group enhancement is relatively sensitive to electrostatics. These data are entirely consistent with the aggregate findings discussed above.

Comparison of CH₄ Uptake in MOFs As Predicted by Different Force Fields. Beyond CO₂ capture and separation, there is considerable interest in employing high-throughput screening to design MOFs optimized for high-pressure methane storage.²⁸ We have thus conducted a similar analysis to the above, computing methane uptake at 298 K, 30 bar and examined sensitivity to different force fields (qualitative conclusions at 100 bar are analogous but are omitted for brevity). Electrostatic interactions are generally negligible for methane and are omitted. The vDW interactions of a particular force field therefore completely determine the predicted methane uptake. We compare the prototypical UFF/TraPPE force field combination to SAPT-FF force field, comparing uptakes over our set of MOFs. All reported values are given in absolute uptake (volume of gas at STP adsorbed per volume of MOF).

The predicted methane uptake values at 298 K, 30 bar are compared in Figure 9. Note that while the CO₂ uptake at 0.2 bar spanned 2 orders of magnitude across the database of MOFs, the high-pressure CH₄ uptake values of the MOFs are within a factor of 4. One should thus expect lower correlation coefficients (at least SRCC) than for the CO₂ uptake. However, the correlation between force field predictions remains strong (SRCC² = 0.81, R² = 0.90), and the slope of the best fit line is very close to one (1.04), indicating that UFF/TraPPE should be a solid choice for high-throughput screening of MOFs for high-pressure methane adsorption. The good agreement between force fields may not be surprising, as it has previously been shown that high-pressure methane uptake in MOFs is strongly correlated to the volumetric surface area and void fraction,²⁷ properties that are relatively insensitive to the details of the force field.

In order to gain deeper insight, we also examined the low-pressure portion of the 298 K isotherm at 1 bar (Figure 10). As evidenced by the slope of the best fit line (1.16), UFF/TraPPE generally predicts higher CH₄ uptake (at 1 bar) than SAPT-FF. This is analogous to our findings for CO₂ uptake, in which the treatment of adsorbate—MOF vDW interactions in the Lennard-Jones type force field led to a systematic prediction of higher gas uptake. On the basis of that analysis, we could anticipate that MOFs with smaller pores (and thus higher density of framework atoms) would exhibit larger deviations. In Figure 11, we compare the fractional deviation in uptake versus free volume fraction of the MOF (calculated as the He accessible free volume²⁷), reflecting the expected trend. Similar to low-pressure CO₂ uptake, we find that low-pressure CH₄ uptake in ZIFs is highly sensitive to the choice of force field,
with UFF/TraPPE predicting 100—200% higher uptake than SAPT-FF for certain ZIFs. The observation that generic force fields significantly overpredict CH4 uptake in ZIFs has been previously demonstrated.46,48 We attribute this to the fact that the ZIFs studied have relatively low free volume, with spherical or cylindrical pores, leading to many nonlocal interactions between adsorbed gas molecules and the atoms of the pore walls of the ZIF and compounding the overestimation of dispersion interactions.

**CONCLUDING REMARKS**

Based upon merely a review of the recent literature, it is difficult to draw a uniform conclusion about the ability of generic force fields to accurately predict gas adsorption over a diverse set of MOFs: comparisons are often made for only a single MOF or sometimes involve "optimized" (i.e., adjusted to reproduce experimental results) force fields or utilize different vdW cutoffs, making it difficult to assess the reliability and robustness of standard force fields for high-throughput screening. In the present work, we circumvent this problem by comparing, for a diverse set of MOFs, against accurate "benchmark" ab initio force fields (SAPT-FF), which contain no empirical parameters and have been shown to semiquantitatively to quantitatively reproduce observed gas uptake on a diverse set of MOFs.

While gas uptake at high pressure seems to be relatively insensitive to the details of the force field (assuming accurate adsorbate—adsorbate potentials), screening low-pressure uptake places far more significant demands on the MOF—adsorbate potential. The relative accuracy of standard force fields depends on the type of adsorbate as well as the topology and functionalization of the MOF. For small, nonpolarizable adsorbates, adsorbed in very open, porous MOFs, standard force fields may predict uptake with good accuracy (our results give ~20% deviations for methane uptake in MOFs with >85% free volume). As the size of the adsorbate molecule increases, and the free volume of a MOF (porosity) decreases, the number of pairwise asymptotic dispersion interactions between adsorbate and MOF increases, and differences in the long-range tail of the vdW interactions of different force fields accumulate in the total adsorption energy. The effective C6 coefficients of Lennard-Jones force fields are generally 30—40% too large compared to the correct asymptotic dispersion interaction, causing the overprediction of methane uptake in MOFs of lower free volume. For larger adsorbates such as CO2, these quantitative deviations are magnified; however, this effect may be obscured by the neglect of explicit polarization. While polarization and vdW interactions have distinctly different effects on the adsorption site profile of a MOF, nonpolarizable Lennard-Jones force fields may benefit from error cancellation by neglecting the former interactions.

In spite of these quantitative differences, we generally find good correlation between the relative ranking of MOFs in terms of absolute gas uptake, as predicted by different force fields. For a high-throughput screening study, with the goal of identifying the top percentage of MOFs for a particular gas adsorption application, it may therefore be a reasonable approximation to employ generic force fields. But caution is still warranted. First, our set of hypothetical MOFs only encompasses three different topologies pcu, fcu, and ftw (in addition to the eight ZIFs, encompassing three additional topologies). In addition, the cancellation of errors from overestimation of dispersion and neglect of polarization is certainly not universal and, in fact, manifests itself in significant differences in the adsorbate probability density between standard and the ab initio force fields. These results suggest the very real possibility for significant breakdowns in at least particular classes of MOFs. We note that our study has focused on relatively nonpolar adsorbates (CH4 and CO2), and it is possible that some of the results/conclusions may not generalize to extremely polar adsorbates (e.g., H2O).

Finally, it is interesting to note the general trend of high correlation coefficients between force field predictions, in spite of sometimes large and systematic quantitative deviations in predicted uptake (in particular for CO2). This may be best exemplified by the comparison of predicted CO2 uptake with and without charges (Figure 2); analogous trends were found by Kadantsev et al.35 A priori, it is extremely surprising that such good correlation in predicted CO2 uptake between force fields exists even after completely eliminating electrostatic interactions, which constitute a major component of the MOF—CO2 interaction. The explanation lies in the fact that the low-pressure CO2 adsorption of the set of hypothetical MOFs spans almost 2 orders of magnitude, with the gas uptake of particular MOFs largely predetermined by their topology and porosity, regardless of their particular functionalization. This has important implications for future high-throughput screening applications, as it should be possible to intelligently prescreen a large database of MOFs using descriptors based on detailed structural characteristics of the MOF, before any simulations are run; indeed, such a procedure has been successfully recently demonstrated.7,10
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REFERENCES


