Performance of van der Waals Corrected Functionals for Guest Adsorption in the M_2(dobdc) Metal–Organic Frameworks

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Supporting Information

ABSTRACT: Small-molecule binding in metal–organic frameworks (MOFs) can be accurately studied both experimentally and computationally, provided the proper tools are employed. Herein, we compare and contrast properties associated with guest binding by means of density functional theory (DFT) calculations using nine different functionals for the M_2(dobdc) (dobdc = 2,5-dioxido,1,4-benzenedicarboxylate) series, where M = Mg, Mn, Fe, Co, Ni, Cu, and Zn. Additionally, we perform Quantum Monte Carlo (QMC) calculations for one system to determine if this method can be used to assess the performance of DFT. We also make comparisons with previously published experimental results for carbon dioxide and water and present new methane neutron powder diffraction (NPD) data for further comparison. All of the functionals are able to predict the experimental variation in the binding energy from one metal to the next; however, the interpretation of the performance of the functionals depends on which value is taken as the reference. On the one hand, if we compare against experimental values, we would conclude that the optB86b-vdW and optB88-vdW functionals systematically overestimate the binding strength, while the second generation of van der Waals (vdW) nonlocal functionals (vdw-DF2 and rev-vdW-DF2) correct for this providing a good description of binding energies. On the other hand, if the QMC calculation is taken as the reference then all of the nonlocal functionals yield results that fall just outside the error of the higher-level calculation. The empirically corrected vdW functionals are in reasonable agreement with experimental heat of adsorptions but under bind when compared with QMC, while Perdew–Burke–Ernzerhof fails by more than 20 kJ/mol regardless of which reference is employed. All of the functionals, with the exception of vdw-DF2, predict reasonable framework and guest binding geometries when compared with NPD measurements. The newest of the functionals considered, rev-vdW-DF2, should be used in place of vdw-DF2, as it yields improved bond distances with similar quality binding energies.

1. INTRODUCTION

Metal–organic frameworks (MOFs) are highly promising materials for gas storage and gas separations due to their crystallinity, high porosity, and tunability. Indeed, the vast number of

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combinations of organic linkers and metal connectors that can be employed allow one to, in principle, design materials for a wide variety of potential applications.\textsuperscript{1,2,3} Unlike other classes of porous materials, MOFs can be synthesized and designed using insights from coordination chemistry. In recent years, a wide variety of coordination solids and MOFs have been made. In many cases, the goal is to design materials with binding pockets tuned to selectively bind one guest (e.g., storage applications) or that favor the adsorption of one guest over another (e.g., separations). From this perspective, it is essential to understand how the framework and the guest interact. Diffraction experiments and simulation can play an important role in developing this understanding.\textsuperscript{3}

Classical methods have played a crucial role in this regard. Gas adsorption can be modeled using Monte Carlo simulations where thermodynamic properties (most often the heat of adsorption and the loading of guest molecules at a given temperature and pressure) are calculated as an ensemble average.\textsuperscript{4,5} This is particularly important, since gas molecules generally physisorb in the MOF and at finite temperatures can access many binding configurations. Additionally, molecular dynamics simulations have been applied to study the framework and the motion of small molecules in MOFs, including the calculation of diffusion constants.\textsuperscript{6,7} Classical force fields have been developed specifically for treating guest binding in MOFs and for the bonding interactions within the frameworks.\textsuperscript{8,9} These force fields as well as semiempirical methods have been used to optimize framework geometries, particularly when breathing motions in MOFs are important or when a large database of MOFs is studied and optimizations with higher levels of theory are intractable.\textsuperscript{9–11}

However, electronic structure methods are best suited to study a smaller number of materials with a focus on understanding the molecular level details of guest binding at the primary binding site (or sites) in MOFs. The ability of density functional theory (DFT) to balance accuracy and computational efficiency has led to its widespread use in electronic structure theory, whether for molecular systems, solids, surfaces, or in this case porous materials. Given the large size of the unit cells of most MOFs, DFT is the quantum chemical method most suitable for routine calculations on the periodic structure of MOFs. However, as is always the case with DFT, the accuracy depends on the exchange-correlation functional that is employed.

In porous materials where guest molecules generally interact with the surface through physisorption, dispersion interactions can dominate substrate binding. A well-known drawback of conventional Local Density Approximation (LDA) or Generalized Gradient Approximation (GGA) functionals is their inability to describe properly the London dispersion forces that originate from nonlocal electron correlation.\textsuperscript{12–17} Fortunately, much work has been accomplished in the DFT community to properly account for such weak interactions using a variety of approaches.\textsuperscript{12–17} One class of functionals is the van der Waals (vdW) inclusive functional developed originally by Langreth, Lunqvist, and co-workers (the so-called DF functionals) and the second-generation version of this functional (the so-called DF2 functionals).\textsuperscript{18,19} A second class of functionals are those that account for dispersion forces through empirical van der Waals correction approaches (the so-called –D Functionals), such as those developed by Grimme and co-workers, and a third class are certain parametrized meta-GGA functionals that have been shown to recover dispersion.\textsuperscript{20} MOFs have been successfully studied for a variety of applications, using each of these three classes of functionals (DF/DF2, –D, and meta-GGA).

However, in most studies the chemistry of the specific materials being considered has been the main focus rather than understanding the performance of the various DFT functionals used. Therefore, in the current study we chose a set of functionals to be representative of these three classes of functionals and focused on understanding their performance in terms of binding for a set of small molecules. There are, of course, many other promising functionals that have been developed to treat dispersion interactions, and so our study is by no means all-inclusive.\textsuperscript{12–17,21–23}

Few MOFs are as well-studied, both computationally and experimentally, as the M\textsubscript{2}(dobdc) family (Figure 1), which is also referred to as M-MOF-74, CPO-27-M, or M\textsubscript{2}(dtbp), where M = Mg, Mn, Fe, Co, Ni, Cu, or Zn.\textsuperscript{24–31} These frameworks have open metal sites to which adsorbates can bind strongly, allowing the effect of changing the metal to be studied systematically. Recently, the manner in which a wide variety of small molecules bind in M\textsubscript{2}(dobdc) was studied with DFT for first-row transition metals, for both the experimentally characterized materials (M = Mg, Mn, Fe, Co, Ni, Cu, or Zn) and some that have not yet been realized (M = Ti, V, or Cr).\textsuperscript{32} In this earlier study by Lee et al.,\textsuperscript{33} it was noted that, while many M\textsubscript{2}(dobdc) compounds have been investigated computationally, several levels of theory have been employed, making a direct comparison between studies difficult. Specifically, Lee et al. optimized the frameworks using the Perdew–Burke–Ernzerhof (PBE) functional,\textsuperscript{32} while the vdW-DF2 functional\textsuperscript{19} was employed to treat the weak binding of a series of guests with the framework for all metal cations M. Their aim was to develop a comprehensive data set as a basis for future comparisons. While this previous study by some of the authors used one level of theory to understand how guest binding changes across a spectrum of small molecules, in this work, we focus on how a select number of dispersion functionals perform for three guests, namely, H\textsubscript{2}O, CO\textsubscript{2}, and CH\textsubscript{4}—molecules for which several other groups have computed adsorption energies in the M\textsubscript{2}(dobdc) series. For example, Lee et al. and Canepa et al. studied water adsorption,\textsuperscript{33,35} while Lee et al., Canepa et al., and Rana et al. studied methane adsorption with...
nonlocal density functionals. Sillar et al. studied methane adsorption using the so-called hybrid MP2/cbs-DFT+D + ΔCCSD(T) approach, where binding energies are computed using periodic empirical dispersion-corrected DFT (a −D functional) but are corrected by second-order Möller−Plesset perturbation theory (MP2) calculations and coupled cluster calculations with single and double excitations and perturbative treatment of triple excitations (CCSD(T)) on finite-sized models. CO$_2$ is by far the most studied guest in the M$_2$(dobdc) framework with a wide variety of density functionals. Cluster models have also been used to study both CO$_2$ and CH$_4$. Overall, what is most notable when looking at the data in the literature is the deviations among the reported energies. For example, the CO$_2$ binding energies reported for Mg$_2$(dobdc), excluding data for GGAs without vDW corrections, range from 41.2 to 62.1 kJ/mol for electronic binding energies and from 37.4 to 58.3 kJ/mol for enthalpies.

Experimental data can provide a reference for calculated energies and structures. In this work, we use published heat of adsorption data as a reference for DFT energies and published neutron powder diffraction (NPD) data as a reference for the DFT-optimized framework geometries as well as the geometries of CO$_2$ and H$_2$O bound in the MOF. For CH$_4$, no NPD data was available and was generated as part of this work. Comparisons with experiment are very helpful, but we wish to emphasize that challenges in the characterization of the materials, structural defects, and thermal effects can make the comparison between experiment and simulation indirect. Therefore, high-level Quantum Monte Carlo (QMC) calculations were also performed to study CO$_2$ binding in the Fe$_2$(dobdc) framework with the goal of evaluating the utility QMC as a high-level reference for the performance of the various DFT functionals. In the following, we will show the performance of nine functionals for three guests (CH$_4$, CO$_2$, and H$_2$O) that were chosen for this study, since they represent a range of binding strengths.

2. COMPUTATIONAL DETAILS

2.1. Periodic Density Functional Theory. In this work, we compare the performance of eight vDW density functionals and the PBE functional, as an example of a standard GGA, for small-molecule binding in the M$_2$(dobdc) framework. This framework consists of a divalent metal connector (M = Mg, Mn, Fe, Co, Ni, Cu, or Zn) and 2,5-dioxido-1,4-benzenedicarboxylate (dobdc$^{-}$) as the linker (see Figure 1). Specifically, we will explore the performance of the DF functionals: optB88-vdW$^{18,53}$ and optB86b-vdW$^{18,54}$ the DF2 functionals: vDW-DF2$^{38}$ and rev-vdW-DF2$^{19,55}$ the −D functionals: PBE-D2$^{52,56}$ PBE-D3$^{52,57}$ and PBE-D3 Bj$^{52,57,58}$ and one meta-GGA functional: M06-L$^{59,60}$ Although all belong to the group of GGA functionals, they generally differ in the nature of the correction that is additionally integrated to include London dispersion interactions. As an aside, the vDW-DF2 functional is known to overestimate bond and lattice distances; therefore, the rev-vdW-DF2 functional was recently developed by Hamada with the purpose of improving the geometries of vdw-DF2. All periodic DFT calculations were performed with the Vienna Ab Initio Simulation Package (VASP) with a plane-wave basis set and projector augmented wave (PAW) potentials, where C (2s2p), O (2s2p), Mg (3s), Mn (4s3d), Fe (3d), Co (4s3d), Ni (4s3d), Cu (4s3d), and Zn (4s3d) electrons were included explicitly in the valence. For the calculations performed on Fe$_2$(dobdc) with the PBE-D3-based functionals, the semicore p-states were also treated as valence states, Fe (4s3d3p).
all atoms) was optimized with each functional using a plane-wave cutoff of 550 eV with forces converged to 0.02 eV/Å. Single-point energy calculations with a higher cutoff of 1000 eV were used when computing the electronic binding energies. The Π-point sampling of reciprocal space was used in all calculations. Tests were again performed with the optB88-vdW functional. The effect of changing the k-point mesh (Table S13) and the cutoff (Tables S13–S16) on the electronic binding energy is given as Supporting Information. The effect is within a kilojoule per mole, with the one exception of PBE-D3; therefore, the higher cutoff 1000 eV will only be used in optimizations with the PBE-D3 functionals. Finally, M06-L calculations were only performed for Mg and Zn (closed-shell cases), since the self-consistent field (SCF) convergence in VASP is challenging, and the calculations are time intensive.

Also in Section 4.3, the heat of adsorption values measured experimentally are enthalpies, but electronic binding energies were calculated. To calculate the heat of adsorption, thermal corrections were computed, and these corrections were ~4 kJ/mol for CO2, 5 kJ/mol for CH4, and 6 kJ/mol for H2O (see Table S17 for exact values). To make the comparison between experiment and theory, we subtracted the vdW-DF2 (see Table S17 for exact values). To make the comparison between experiment and theory, we subtracted the vdW-DF2 calculations with which to compare the DFT results. Further-
functions varies depending on the metal or binding strength of the guest.

4.1. Comparison of DFT Results with Quantum Monte Carlo in Fe₂(dobdc). Although a significant amount of experimental data is available for the M₁₅(dobdc) series, electronic structure methods can be performed for systems independent of experiment, in addition to providing complementary data in collaborative studies. Furthermore, as has often been discussed in the literature, making comparisons between experiment and simulation for porous materials is not always straightforward. Differences between experimental geometries and errors intrinsic in measurements can lead to indirect comparisons. Additionally, experimental measurements are of binding enthalpies, and calculating enthalpies requires including thermal effects. While outside the scope of this work, research into accurately computing the vibrational contributions to the enthalpy, in particular, anharmonic effects, is another active area of research, and the use of the harmonic approximation in this work may contribute to some of the differences between our calculations and experiment. Since this work is focused on how different DFT functionals treat the electronic contributions to the enthalpy of adsorption, a higher-level quantum chemical method could be used to compute electronic binding energies that can be directly compared to DFT electronic binding energies. With this in mind, QMC calculations were performed for CO₂ in Fe₂(dobdc) to determine the viability of this approach to determine the accuracy of the DFT binding energies. Since geometry optimizations for the system sizes being considered here are beyond reach with QMC, structures were taken from DFT, as is common practice in QMC-based determinations of binding energies (see Al-Hamdani et al. and Ma et al.). So as to get a clean comparison with the DFT functionals, binding energy calculations were repeated for each functional at the same geometry used in the QMC calculations. The results obtained from these calculations are reported in Table 1. The QMC estimate of the binding energy is ca. 40–45 kJ/mol; specifically, two values of 44.0 ± 2.0 and 41.0 ± 2.0 kJ/mol have been obtained depending on how finite size effects are taken into account. In the former, finite size effects were corrected for with the method of Chiesa et al. and in the latter the model periodic Coulomb (MPC) interaction approach was used.

Because of the size of the unit cell being considered and the enormous associated computational cost of the QMC simulations, explicit convergence tests in larger unit cells are beyond reach, and so we do not attempt to discriminate between the two values obtained.

Turning to the comparison between QMC and DFT, we find that PBE performs poorly and underestimates the binding energy by more than 20 kJ/mol. This is consistent with general understanding that standard GGAs such as PBE do not properly account for dispersion. All of the van der Waals inclusive functionals do significantly better. On the one hand, the DF functionals are 1–2 kJ/mol below the lower end of the range predicted by QMC. On the other hand, the DF2 functionals fall on the other end of the QMC predicted range and bind 3–5 kJ/mol weaker than the upper end of the QMC range. The −D functionals also bind weaker than the upper end of the QMC range by 6–8 kJ/mol. In Table 1, we also included results (taken from Section 4.3) where the position of CO₂ was optimized with each functional. These data are included here to demonstrate the effect of using a fixed geometry in DFT with the goal of providing some indication of the potential effect of not optimizing with QMC. These calculations show that at the DFT level changes in structures lead to at most ∼1 kJ/mol change in binding energy. The differences in binding energy between the respective are larger than this; therefore, we expect the use of the fixed geometry to have a limited impact on the interpretation of our results.

Before closing, it is essential to compare the QMC value to the experimentally determined result. From the work of Queen et al., a value of −33.2 kJ/mol has been obtained for CO₂ in Fe₂(dobdc). Adjusting this experimental value by adding an estimated 3.616 kJ/mol for finite temperature and zero-point energy (ZPE) effects leads to value of −36.8 kJ/mol. This is quite close but nonetheless slightly (4 to 7 kJ/mol) lower than the QMC estimated value of ca. 40–45 kJ/mol. It is beyond the scope of the current study to resolve this discrepancy, but doing so would make interesting work for the future. On the QMC side, it will require a careful consideration of finite size effects, timestep errors, and potential sensitivity of the results to the nature of the trial wave function or the geometry; however, the thermal corrections to the energy computed with DFT use the harmonic approximation, and this could contribute to the differences as well.

The importance of the choice of reference can already been seen. On the one hand, if the experimental value is used as the reference, the DF functionals over bind by ∼8 kJ/mol, while the vDHF functional under binds by only 1.3 kJ/mol. On the other hand, the rev-vDHF functional under binds by only 0.4 kJ/mol, and the −D functionals are under binding by 1–3 kJ/mol (as opposed to 6–8 when compared to QMC). We again wish to emphasize that care must be taken when assigning the “best” functional if comparing only against experiment or only against another computational method such as QMC.

4.2. The Effect of the vDHF Treatment on the Framework Geometry. In Section 4.1, we explored the effect of changing the computational method while keeping the geometry fixed. In this section, we will study the effect changing the computational method has on the optimized geometry of the framework. In the previous section, we used the PBE geometry of Lee et al. They compared the calculated PBE lattice constants and metal—oxygen distances with neutron and X-ray diffraction measurements as well as with other calculated values previously reported in the literature. In the diffraction experiments,
temperatures ranged from 4 to 368 K depending on the experiment. Although in several cases, the temperature is very low, note that the DFT calculations are performed at 0 K, and thermal and zero-point effects can thus contribute to the differences between the measured and calculated values. Here we compare our results with the measurements made at the lowest temperature (see Table 2 and Table S1). 34,26,27,31,76,89,90 Two important trends are considered here: the effect on the geometric parameters when the metal is changed and the performance of each functional compared to experiment (and one another). Note that the optimizations were performed using the rhombohedral unit cell, but they have been converted to the conventional trigonal cell for comparison with experimental results below.

The lattice parameters and M−O bond distances change depending on the metal in the framework. In Figure 2, all of the functionals studied here can reproduce the general experimental ordering across the metals for both lattice constants and bond distances. The ordering in the lattice parameter a is Mn > Fe > Cu > Mg > Zn > Co > Ni, the ordering in the lattice parameter c is Mn > Mg > Fe > Zn > Co > Ni > Cu, the ordering in the apical M−O bond distance is Cu > Zn > Mn > Mg > Fe > Co > Ni, and the ordering in the basal M−O distance is Zn > Mn > Fe > Mg > Co > Ni > Cu. For cases where the differences between the experimental values is small, the ordering of two metals may deviate from those listed above for some functionals (i.e., the average basal M−O distances for Ni and Cu are very close). If we take Mg2(dobdc) as an example, the performance of the functionals for framework geometries can be observed. A complete list of geometric parameters is given in Table S1. The framework geometry optimized with the PBE functional has been compared to a larger set of experimental data by Lee et al. 33 For the Mg framework with the experimental reference taken in this work by Liu et al., 34 PBE deviates from experiment by 0.57% in lattice constant a and by 0.97% in lattice constant c. Aside from M06-L, all of the functionals yield larger lattice constants than experiment. On the one hand, for the functional with values closest to experiment (for Mg, PBE-D2), the lattice constant has a percent deviation from experiment of 0.34%, while the c constant deviates by 2.60%. On the other hand, the vdW-DF2 functional deviates by 1.11% in a and 1.28% in c and is the farthest from experiment. M06-L has percent deviations of 0.54% in a and 0.47% in c, but the lattice constants are shorter than those of experiment. The remaining vdW functionals all do reasonably well and have deviations between 0.34 and 0.46% in a and 0.55−0.84% in c.

If we use the percent deviation from experiment to characterize how well the functionals describe the Mg−O apical bond, we would determine that M06-L does the worst, as it deviates by 4.33%, while vdW-DF2 does the best deviating by 1.92%. This is a clear example of why we recommend taking care when making comparisons with one experimental measurement (in this case, a single distance from one experimental structure). The vdW-DF2 functional (one of the DF2 functionals) not only overestimates bond distances in our systems (Figure 2) but has been shown to do so in a variety of chemical systems. 32 The fact that it is closest to experiment raises suspicion and is likely due to an elongated Mg−O apical bond. In fact, it is known that only ~80% of the metal sites are accessible for small-molecule binding in the Mg2(dobdc) structure. 38

However, we can still use percent deviations as a guide if we take the PBE functional as a reference, since it has been previously shown to do reasonably well for metal−oxygen distances in this framework. On the one hand, M06-L predicts shorter bond distances and deviates from PBE by 1.5% for both the apical and basal distances. On the other hand, the PBE-D2, PBE-D3 BJ, optB88-vdW, optB86b-vdW, vdw-DF2, rev-vdw-DF2, PBE-D2, PBE-D3, PBE-D3 BJ, and M06-L

| Method         | Lattice Constant (Å) | Mg−O Apical Distance (Å) |
|----------------|----------------------|---------------------------|
|                | a                    | c                         | apical         | basal         |
| exp (ND at 20 K)99 | 25.921(2)            | 6.8625(8)                 | 2.08           | 2.01          |
| PBE            | 26.07                | 6.93                      | 2.02           | 2.04          |
| optB88-vdW     | 26.03                | 6.91                      | 2.03           | 2.04          |
| optB86b-vdW    | 26.01                | 6.90                      | 2.02           | 2.03          |
| vdw-DF2        | 26.21                | 6.95                      | 2.04           | 2.05          |
| rev-vdw-DF2    | 26.01                | 6.91                      | 2.02           | 2.03          |
| PBE-D2         | 26.01                | 6.88                      | 2.02           | 2.04          |
| PBE-D3         | 26.04                | 6.92                      | 2.02           | 2.02          |
| PBE-D3 BJ      | 26.03                | 6.91                      | 2.02           | 2.04          |
| M06-L          | 25.78                | 6.83                      | 1.99           | 2.01          |

“The primitive cell used for the calculations was converted to a conventional cell to compare with experiment. The basal Mg−O bond distances are the average of all four basal Mg−O bonds.

4.3. The Effect of the vdW Treatment on the Binding Energies and Guest Geometries. In this section, we explore the effect changing the computational method has on the binding energy and guest binding geometries. Since high-quality experimental data are a prerequisite for assessing the performance of the calculations in this section, before discussing our results we first introduce the structural data to which we will make comparisons. While NPD experiments had been reported for CO2 in the M2(dobdc) series, 43 CH4 adsorption had not been measured. To characterize the coordination of the methane molecule at the metal site, NPD experiments were performed by dosing each of the M2(dobdc) materials with CD4. An amount corresponding to 0.75 CD4 molecules per metal atom was chosen to ensure that all of the gas would preferentially adsorb at the metal site without any adsorption at secondary sites. Fourier difference maps generated during the refinement process confirmed...
that all residual nuclear density was indeed located exclusively above the metal centers.

Figure 3 shows the local coordination of the CD$_4$ molecule adsorbed at the metal site for each of the materials, and the interaction distances are listed in Table 3. For all of the materials, the CD$_4$ molecule binds with a nearly identical geometry, where the metal interacts with three of the D atoms of the molecule, and the fourth is aligned nearly perpendicular to the basal plane. A slight tilting of the molecule is observed in the Co$_2$(dobdc) and Ni$_2$(dobdc) structures, where closer contacts with two of the D atoms occurs compared to the other materials. This tilting does not result in a closer metal–carbon distance, as the values for Mg$_2$(dobdc), Mn$_2$(dobdc), Fe$_2$(dobdc), Co$_2$(dobdc), and Ni$_2$(dobdc) all fall within 2.90 and 2.95 Å. Longer interaction distances are observed, as expected, for Zn$_2$(dobdc) and Cu$_2$(dobdc), where the metal–carbon distances increase to 3.09(1) and 3.28(1) Å, respectively. These observations correlate with long metal–gas interactions reported recently for CO and CO$_2$ in Zn$_2$(dobdc) and Cu$_2$(dobdc) compared to the rest of the series, as well as with the DFT calculations presented herein.$^{43,91}$

Along with the experimental structural data, experimental heats of adsorption are available for both CO$_2$ and CH$_4$. By comparing the measured and calculated binding energies (Figure 4a,b), we find that all of the functionals yield the correct metal dependence for guest binding. The trend in binding energies that is observed across the M$_2$(dobdc) series has been explained for CO$_2$ in previous studies, such as those by Lee et al. and Poloni et al.$^{33,84}$ The CO$_2$ molecule bends slightly upon binding at the open-metal site thereby obtaining a dipole moment. Furthermore, the strength of binding between CO$_2$ and the open metal center is not only due to a strong electrostatic interaction but also through the hybridization between the metal d$_z^2$ orbital and a lone pair on CO$_2$. For Mn through Co, the d$_z^2$ orbital is singly occupied; however, in Cu and Zn this orbital is doubly occupied, and the binding strength decreases. While no experimental data are available for H$_2$O (Figure 4c), all of the functionals show the same metal dependence when compared to one another and following a trend similar to that of CO$_2$. Additionally, since CH$_4$ binds weaker and does not have a dipole, it is not surprising that the metal dependence is smaller with only Cu showing a significant difference in binding strength.
The functionals were first compared with experimental binding energies (note that PBE was not included in this section, since the performance in Section 4.1 was so poor). The DF functionals overbind when compared to experiment (see Figure 4); however, binding energies improve for the DF2 functionals (see Section 4 of the Supporting Information for a discussion of an energy decomposition showing the differences arising from the vDW term). Furthermore, the CO2 binding energies for the two DF2 functionals differ at most by 2.7 kJ/mol across the metal series, and the two DF functionals differ at most by 0.6 kJ/mol. The two sets differ from one another by ∼9 kJ/mol. Although the difference in methane binding energies predicted between the two DF2 functionals remains small, rev-vdW-DF2 consistently predicts the binding energy to be ∼3 kJ/mol weaker than vDW-DF2. This is also the case for the DF functionals, where optB88-vdW binds only very slightly weaker than optB86b-vdW for methane.

However, the −D functionals without Becke–Johnson (BJ) damping under bind for CO2 and over bind for methane when compared with experiment. For CO2 and H2O, their performance is more similar to the DF2 functionals, while for methane their performance is between that of the DF and DF2 functionals. PBE-D3 BJ exhibits results very similar to the other −D and DF2 functionals for CO2 and H2O2; however, it remains close to the DF2 functionals for methane, while the other −D functionals bind stronger.

Finally, the M06-L binding energies for CO2 and CH4 are in reasonably good agreement with experiment but bind slightly stronger than the DF2 functionals. While this functional performed well across the board, the M06-L calculations required significantly more wall time than the other functionals tested herein, and SCF convergence was challenging.

![Table 3. Metal–Carbon Distance and the Average of the Three Closest Metal–Deuterium Distances for the Methane Molecule Adsorbed at the Metal Site from the M2(dobdc)·1.5CD4 Structures Measured at 8 K](image)

| metal | Mg | Mn | Fe | Co | Ni | Cu | Zn |
|-------|----|----|----|----|----|----|----|
| M–C (Å) | 2.95(2) | 2.93(3) | 2.90(3) | 2.95(3) | 2.95(1) | 3.28(1) | 3.09(1) |
| M–D avg (Å) | 2.79(3) | 2.77(5) | 2.78(4) | 2.80(5) | 2.79(2) | 3.10(2) | 2.92(3) |

![Figure 4. Electronic binding energies for eight functionals in the M2(dobdc) series and available experimental data. To compare the experimental heat of adsorption 43,81 with the calculated electronic binding energy, the harmonic vibrational corrections computed with the vdw-DF2 functional were subtracted from the experimental value for each case. The upper panels (a–c) show absolute values for CO2, CH4, and H2O, respectively. The lower panels in (a, b) indicate the relative differences to the experimental values.](image)
The final measured and calculated property to be compared is the binding geometry of the guests. The selected parameters used to describe guest binding are the distances $M\text{−}OCO_2$, $M\text{−}CCH_4$, and $M\text{−}OH_2O$ (Figure 5). Although we did not have experimental heats of adsorption for $H_2O$, the $M\text{−}OH_2O$ distance was previously reported for $Co_2(dobdc)$ at 100 K using single-crystal X-ray diffraction (XRD). The experimental distance of 2.137(0) Å is included as well.

As was the case with the lattice parameters, the DF functionals, rev-vdW-DF2, and M06-L have guest binding distances in better agreement with experimental data from NPD than the vdW-DF2 functional and, in this case, to some extent the empirically corrected ones (Figure 5). We again take $Mg_2(dobdc)$ as an example to demonstrate this point (Figure 5a,b). The experimental distances for guest binding are 2.270 Å for $CO_2$ and 2.952 Å for $CH_4$. On the one hand, the functionals that perform well (the DF functionals, rev-vdW-DF2, and M06-L) have percent deviations from experiment between 3.00 and 3.88% for $CO_2$ and 0.07–0.88% for $CH_4$. On the other hand, the vdW-DF2 functional results in the longest bond distances between metal and guest for all of the studied cases with percent deviations from experiment of 6.17% and 5.22% for $CO_2$ and $CH_4$, respectively. For the −D functionals, PBE-D3 and PBE-D3 BJ have percent deviations of ~6% for $CO_2$ and ~5% for $CH_4$ while PBE-D2 has slightly smaller deviations of 4.36% and 3.14% for $CO_2$ and $CH_4$, respectively. However, as was the case for the binding energies, in Figure 5 we see that the PBE-D2 functional is not consistently the best of the −D functionals (or put another way, the PBE-D3 functionals do not always have long distances like vdW-DF2). Given that the metal–oxygen distances for $CO_2$ binding are overestimated in general with $Zn$ having the largest differences from experiment, we again caution in reading too much into smaller differences between the experimental and calculated geometry for one particular framework. When the difference from experiment is plotted in Figure 5, the most dramatic deviations are for $CH_4$, and it is once more that vdW-DF2 consistently has larger errors than the remainder of the functionals.

While very limited experimental data are available for $H_2O$ binding, recall that $H_2O$ binds stronger than $CO_2$ and consequently, upon $H_2O$ adsorption, the bond between the apical oxygen atom and the metal center is elongated (Figure 5c). Thus, the strong interaction with $H_2O$ results in a weakening of the bond between the metal and the oxygen atom trans to the $H_2O$ within the framework. Additionally, the single-crystal diffraction experiment was performed for a loading higher than one $H_2O$ per metal center; therefore, in the experiment the $H_2O$ interacting to...
the metal is also interacting with neighboring H$_2$O molecules and could contribute to differences between the measured and calculated values. Nevertheless, for H$_2$O in Co$_2$(dobdc) vdW-DF2 again has the largest deviation from experiment.

5. CONCLUSIONS

While it is clear that small-molecule adsorption in MOFs cannot be studied without properly accounting for vdW interactions, multiple functionals are often not applied to systems in the literature. Fortunately, we find that the trends across metals in our system are reproduced with all eight vdW functionals; however, the assignment of a “best” functional is not straightforward.

If we compare with QMC calculations (Section 4.1), a clean comparison of electronic binding energies on identical structures can be made with DFT. These calculations were primarily performed to demonstrate that QMC, despite its enormous computational cost, is now feasible on systems as complex as MOFs thanks to recent developments. For the specific system examined, the QMC results suggest that the DF functionals bound CO$_2$ by an energy between 1 and 2 kJ/mol stronger than examined, the QMC results suggest that the DF functionals energies and geometries. While M06-L was only form reasonably well, in some cases on par with the DF2 functional, while the DF2 functionals correct for this and provide a with experimental heat of adsorption measurements suggest that the DF functional is not straightforward.

The coordinates for DFT-optimized geometries, values of the data plotted in the main text, additional data from DFT convergence tests, and crystal structure details and Rietveld refinement plots (PDF) X-ray crystallographic information, additional data (ZIP)

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