Accurate Ab Initio Description of Adsorption on Coordinatively Unsaturated Cu^{2+} and Fe^{3+} Sites in MOFs

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S *Supporting Information*

ABSTRACT: The performance of different exchange−correlation functionals was evaluated for the description of the interaction of small molecules with (i) cluster models containing Cu^{2+} and Fe^{3+} coordinatively unsaturated metal sites and (ii) HKUST-1 metal organic framework (MOF). Adsorbates forming dispersion-bound complexes (CH_4), complexes with important dispersion and electrostatic contributions (H_2, N_2, CO_2), and complexes stabilized also by a partial dative bond (CO, H_2O, and NH_3) were considered. The interaction with coordinatively unsaturated sites was evaluated with respect to the coupled-cluster calculations for Cu^{2+} and Fe^{3+} centers represented by cluster models. The adsorption on dispersion-stabilized sites was examined for the cage-window and the cage-center sites in HKUST-1 with respect to the experimental and DFT/CC results. None of the functionals considered can accurately describe the interaction of all seven adsorbates with Cu^{2+} and Fe^{3+} sites and with dispersion-dominated adsorption sites. The interaction with coordinatively unsaturated sites was frequently underestimated, for adsorbates forming a partial dative bond in particular, while the adsorption at dispersion-stabilized sites was overestimated. Consequently, interaction energies calculated for different adsorption sites were often in qualitatively incorrect order. The optimal exchange−correlation functional for a particular adsorbate/MOF can thus be found by comparing the performance of various functionals with respect to highly accurate calculations on smaller cluster models as a good representative of MOF structural building blocks.
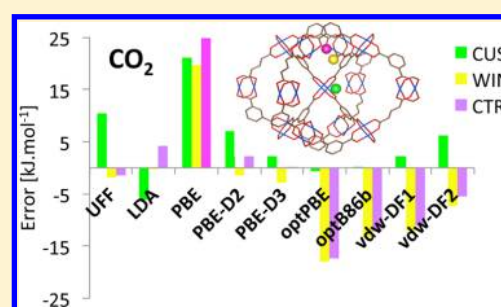
INTRODUCTION

Metal organic frameworks (MOFs) have drawn considerable attention due to their adsorption and even catalytic properties.[1−5] MOFs containing coordinatively unsaturated sites (CUSs) are of particular interest due to their adsorption selectivity and potential catalytic applications.[1−3,5] An improved understanding of the adsorbate−CUS interaction is essential for the design of the optimal adsorbents and catalysts for particular applications. Numerous experimental techniques have been used in the investigation of adsorption on CUSs, including IR and UV−vis spectroscopy, X-ray and neutron diffraction, calorimetry, and the adsorption isotherm measurement,[6−10] and the experimental results were compared with the results of theoretical studies employing a variety of models and methods.[11−14] It is fair to say that the agreement between experimental and theoretical results (and even between various theoretical studies) is often far from perfect, for transition-metal CUSs in particular. It has been shown recently that even seemingly good agreement between theoretical and experimental adsorption isotherms could be based on a qualitatively incorrect adsorption mechanism.[11,15]

An accurate description of adsorbate interactions with CUSs is a significant challenge for computational chemists: (i) the description of CUSs formed by transition-metal cations with a partially filled d shell often requires the use of the multireference wave function; (ii) a spin−spin coupling between unpaired electrons on individual transition-metal cations must be considered; (iii) the dispersion interactions between the adsorbate and MOFs must be treated adequately; and (iv) due to a large size of a unit cell (UC) typical for the majority of MOFs, only the methods based on the density function theory (DFT) are suitable for the description of the electronic structure of these systems. It follows that the choice of a suitable method for a particular adsorbate/MOF system is not straightforward, and different exchange−correlation functionals were used and recommended for diverse systems. While the adsorption on coordinatively unsaturated metal sites (CUSs) has been intensively studied theoretically,[16−20] a systematic theoretical investigation of the DFT performance for the adsorption of various molecules at a variety of adsorption sites in different MOFs is missing.

Different recommendations as for the suitability of exchange−correlation functionals have been given mostly due to the fact

that individual studies have focused only on single (or few) adsorbates, often considering only the CUSs, and a comparison with the adsorption on MOFs containing different transition metals is lacking. Clearly, a systematic investigation carried out for various adsorbates interacting with different types of adsorption sites is missing. It is the purpose of this study to provide such a systematic investigation of the DFT performance; in addition, the transferability and generalization of the conclusions relevant to DFT accuracy from system to system are critically discussed. An improved understanding of accuracy of various density functionals for the description of transition metal-containing MOFs is the major goal of the present investigation. Seven different small molecules as model adsorbates have been considered, and a wide range of different exchange−correlation functionals have been tested. First, the interaction of adsorbates with the cluster model was investigated using the coupled-cluster method extrapolated to the complete basis set limit, CCSD(T)/CBS, as the reference. Cluster models representing Cu^{2+} and Fe^{3+} CUS sites in MOFs were investigated. The transferability of the conclusions obtained for the cluster model was then tested for: (i) the CUS change from Cu^{2+} to Fe^{3+}; (ii) the size and geometry of the model cluster; and (iii) the transition from the cluster model to the periodic model of MOF, considering also other adsorption sites. The performance of density functionals for balanced description of adsorption on the CUS sites and on the dispersion-driven interaction sites (small cages or windows) was investigated for HKUST-1 MOF. The selection of HKUST-1 for the present investigation was motivated by the fact that the interaction between adsorbates and Cu^{2+} CUSs in HKUST-1 has recently been investigated computationally using either a cluster or a periodic model;[13,15,16,18,20−27] and it is also important that relatively large amounts of experimental data are available for HKUST-1, and they can be compared with theoretical results.[7,8,11−13,20,28]

■ METHODS

HKUST-1[29] MOF (Cu_3(1,3,5-benzenetricarboxylate)$_2$, frequently denoted as CuBTC) contains three major adsorption sites: coordinatively unsaturated sites, where molecules interact with the Cu^{2+} cation and the interaction is dominated by electrostatic interactions and by the formation of a partial dative bond and cage-center (CTR) and cage-window (WIN) sites, where the interaction of molecules with organic linkers is dominated by dispersion interactions.[12] This makes the HKUST-1 MOF a particularly suitable system for the evaluation of the method's accuracy since both dispersion-stabilized adsorption complexes and those stabilized mostly by electrostatic interaction and partial dative bonds must be described with similar accuracy. It has been shown that this is of major significance for a proper assessment of the method's accuracy. The three-dimensional CuBTC structure has the main cage and a small tetrahedral cage with a diameter of about 10 and 5 Å, respectively. The Cu^{2+} sites are exposed to the main cage, and the interaction with smaller adsorbates can be investigated with merely a cluster model; therefore, it is possible to employ highly accurate ab initio methods, such as the coupled-cluster method.

The CuBTC structure consists of paddle-wheel units (PDWLs), where two Cu^{2+} cations are charge compensated by four carboxylic groups from trimesic acid. The PDWL cluster model terminated with hydrogen atoms is often used as a model.[13,18,21] The presence of two unpaired electrons on each Cu^{2+} requires the investigation of the system in different electronic states. Using the multireference perturbation theory, it

has been shown for PDWL-H_2O and PDWL-CO complexes that the interaction energy is the same for singlet and triplet electronic states.[13,30] Therefore, the dependence of the interaction energy on a particular spin state should not play an important role, and the interaction energies can be obtained using a well-defined single-reference wave function for the high-spin state. This conclusion opens the possibility of using computationally less demanding single-reference based (e.g., coupled-cluster) methods, and it makes the system suitable for the benchmarking of DFT interaction energies. However, other properties (e.g., magnetic) can be strongly dependent on the local spin configuration of the metal centers in the material.[31] In order to address those properties quantitatively a multireference wave function is usually required.

$Cu(HCOO)_2$ and $Fe(HCOO)_2(OH)$ cluster models (Figure 1a,b, respectively) were used to investigate the adsorption on CUSs in
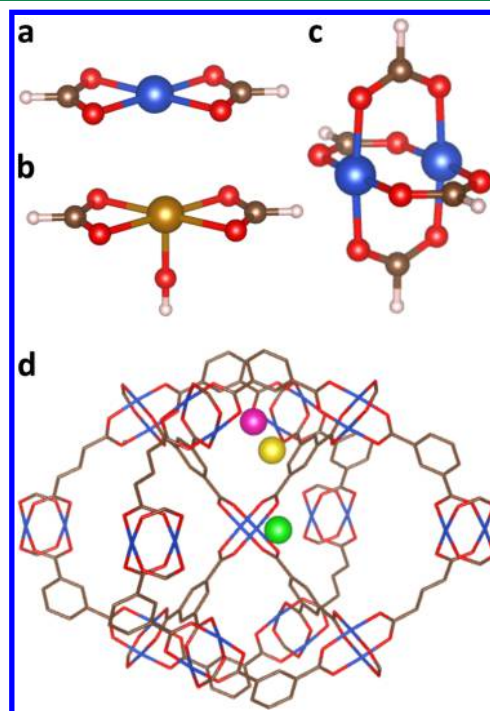
Figure 1. Small cluster models of CUSs and the CuBTC supercage. (a) The planar $Cu(HCOO)_2$ (D_{2h}) cluster model. (b) The Fe-$(HCOO)_2(OH)$ (C_{2v}) cluster model having a planar arrangement of the $Fe(HCOO)_2$ unit with the OH ligand perpendicular to this plane. (c) The paddle-wheel $Cu_2(HCOO)_4$ (D_{2h}) cluster model. (d) The CuBTC supercage; three important adsorption sites are shown as green, yellow, and magenta balls: CUS, tetrahedral WIN, and tetrahedral CTR sites, respectively.

MOFs containing Cu^{2+} (e.g., CuBTC or CPO-27) and Fe^{3+} (e.g., MIL-100 or MIL-127) adsorption sites. The basis set of Peterson et al.[32] (including a pseudopotential) was used for Cu, while standard Dunning's correlation-consistent valence $−X$-ζ basis sets[33] were used for the remaining atoms in the $Cu(HCOO)_2$ cluster model. The Fe was described with relativistic all-electron basis sets as proposed by Balabanov and Peterson,[34] and the remaining atoms of the $Fe(HCOO)_2(OH)$ cluster were described with Dunning's basis set as recontracted by Jong et al.[35] The second-order Douglas−Kroll−Hess Hamiltonian was employed to include relativistic effects. For the sake of brevity, all basis sets used are denoted as VXZ, where X is the cardinal number of the basis set (D, double; T, triple; and Q,

quadruple), and the corresponding augmented basis sets are denoted as AVXZ. The complete basis set (CBS) limit for the correlation part was obtained by means of cardinal number X dependence ($E_X = E_{CBS} + AX^{-3}$)[36] using the basis sets defined in eqs 1 and 2 for $Cu(HCOO)_2$ and $Fe(HCOO)_2(OH)$ clusters, respectively; HF/VQZ was taken as a CBS for the uncorrelated part.

$$CCSD(T)/CBS = CCSD(T)/AVDZ + MP2/CBS - MP2/AVDZ \tag{1}$$

$$CCSD(T)/CBS = CCSD(T)/VTZ + MP2/CBS - MP2/VTZ \tag{2}$$

The reliability of various DFT-based methods for the interaction between adsorbates and CUSs (represented by cluster models) was evaluated with respect to the CCSD(T)/CBS benchmark calculations using the same geometries. The effect of zero-point-vibrational energy (ZPVE) was neglected when discussing the performance of DFT calculations with respect to the reference level of theory. The following DFT functionals were examined: LDA, GGA (PBE, PW91, RPBE, BLYP),[37−41] meta-GGA (TPSS, M06-L),[42,43] hybrid (PBE0, B3LYP, BHLYP, M05-2X),[44−47] and double-hybrid (B2PLYP),[48] long-range corrected BLYP functional (LC-BLYP[49]), empirically corrected functionals (DFT-D2, DFT-D3, DFT/CC),[50−52] and recently developed nonlocal functionals (vdW-DF1, vdW-DF2, optPBE, optB86b).[53−56] The VQZ or AVQZ basis sets were used for all DFT calculations, and all interaction energies were counterpoise corrected (CP).[57] The frozen monomer approximation was employed unless stated otherwise. The $Cu(HCOO)_2$ and $Fe(HCOO)_2OH$ monomers were optimized at the PBE/VTZ and B3LYP/VTZ levels of theory, respectively. The $Fe(HCOO)_2OH$ cluster model was described in high spin sextet electronic state, which was found to be the most stable at CASPT2 level of theory (for more details see Supporting Information). Seven different model adsorbates were considered: CH_4, H_2, N_2, CO_2, CO, H_2O, and NH_3; the geometries of adsorption complexes are given in the Supporting Information.

The water interaction with a larger $Cu_2(HCOO)_4$ cluster model (Figure 1c) in a triplet electronic state was investigated for the subset of the functionals investigated. The geometries from ref 30 were used, interaction energies were CP-corrected, and ZPVE was neglected.

The periodic calculations were performed for the rhombohedral primitive cell of CuBTC ($a = b = c = 18.774$ Å and $\alpha = \beta = \gamma = 60°$) optimized in ref 30. The projector-augmented wave approximation (PAW) with cutoff energy of 600 eV was used. The k-point sampling was restricted to the Γ-point. The nonspin polarized calculations were performed because of their faster convergence. It is noteworthy that in most instances the difference in interaction energies between nonspin polarized and spin polarized high-spin ferromagnetic solution was negligible.[12] All cluster calculations were performed with Molpro[58] or Gaussian09[59] quantum chemistry packages, and periodic calculations were carried out with the VASP[60] code.

■ RESULTS

Cluster-Model Calculations. The small cluster models containing CUSs (Figure 1a,b) enable benchmarking with respect to the CCSD(T)/CBS results. Seven different adsorbates (CH_4, H_2, N_2, CO_2, CO, H_2O and NH_3) were investigated. Those molecules represent different types of adsorbent−adsorbate interactions including dispersion and electrostatic

interactions and partially covalent bonding. The results for the $Cu(HCOO)_2$ cluster model are summarized in Table 1. The corresponding errors are given in Figure 2, and the mean signed error (MSE) and the root-mean-square deviation (RMSD) for all the adsorbates investigated are also reported in Table 1. The MP2/CBS results are reported as well, because the MP2 approach is quite often used as a benchmark for the cluster models of the MOFs containing CUSs.[19,21,61] The coloring scheme used in Table 1 shows easily the performance (i.e., errors) of individual functionals for particular adsorbates; the darker the red or blue color, the larger the error (an underestimation or overestimation, respectively).

The results obtained for the exchange−correlation functionals that do not explicitly include the dispersion correction are discussed first. The majority of these functionals strongly underestimate the interaction energies with respect to the reference CCSD(T)/CBS level of theory, while LDA and M05-2X functionals systematically overestimate the interaction. The exceptions are LC-BLYP and M06-L functionals, which perform quite well. The excellent performance of the meta-GGA M06-L functional (even better than that of MP2) can be attributed to the parametrization procedure, which effectively includes some of the nonlocal correlation into the local functional itself. The similarly parametrized hybrid M05-2X functional, however, does not perform so well, in particular for complexes with a significant electrostatic contribution and a partial dative bond.

Adding the dispersion correction (Table 1) significantly improves the interaction energies for all studied functionals as can be seen by the decreased values of MSE and RMSD (Table 1). The superior performance of the double-hybrid B2PLYP-D functional is apparent (Figure 2). The performance of hybrid functionals augmented with a dispersion term (PBE0-D3 and B3LYP-D3) is good with RMSD values below 3 kJ mol^{-1}. Nevertheless, the performance of nonlocal functionals, for complexes with partial covalent bonding and a significant electrostatic contribution in particular, is rather poor, and the interaction energies are significantly underestimated. Similarly, the accuracy of GGA and meta-GGA functionals augmented by the D3 term for the description of dispersion interactions is unsatisfactory. More detailed analysis of functional performance connected with incorrect charge distribution at DFT level is given in Supporting Information.

The interaction energies of a subset of molecules (CH_4 and CO_2) with the $Fe(HCOOH)_2OH$ cluster model were evaluated for the subset of functionals listed in Table 2; this subset was chosen to represent various levels of DFT approximations and includes functionals which were found to provide reasonable accuracy for the $Cu(HCOOH)_2$ cluster model. In line with a previous observation, the functionals without the dispersion correction (PBE and B3LYP) were found to strongly underestimate the interaction energy. A failure of vdW-DF2 is also quite notable. Several functionals performing well for Cu^{2+} complexes show relatively good accuracy also in the case of the CH_4 interaction with the $Fe(HCOOH)_2OH$ cluster, but none of the functionals can describe the interaction with CO_2 accurately. The error of 5 kJ mol^{-1} found for M06-L, LC-BLYP, and B2LYP-D is nevertheless smaller than the error of MP2.

The transferability with respect to the size of the cluster model was investigated for a subset of functionals representing the individual types of functionals (Table 3). The errors of DFT in the description of the H_2O interaction with the Cu^{2+} CUS with respect to the CCSD(T)/CBS level of theory are reported for

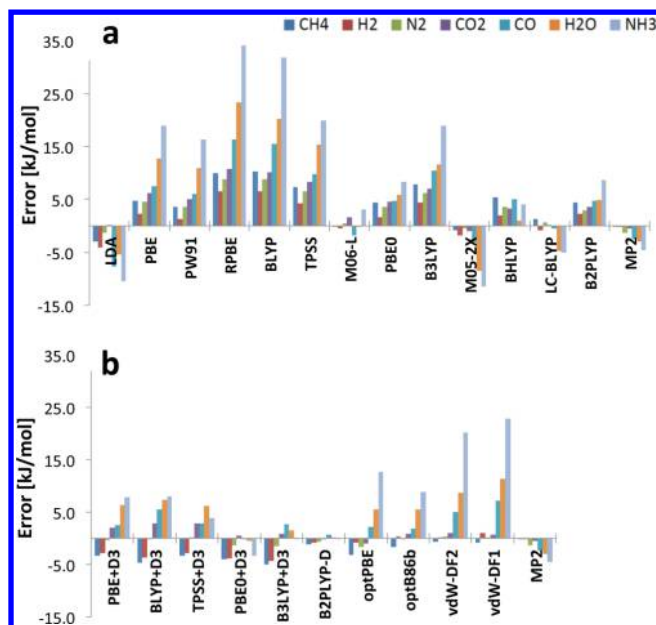**Table 1. Interaction Energies (in kJ mol^{-1}) of the Cu(HCOO)$_2$ Cluster Model and Different Adsorbates Calculated with Various Functionals**[a]

Method	Functional	CH$_4$	H$_2$	N$_2$	CO$_2$	CO	H$_2$O	NH$_3$	MSE	RMSD
					DFT					
LDA	SVWN5	-10.4	-8.9	-8.9	-9.8	-22.3	-33.0	-65.6	-4.5	5.6
GGA	PBE	-2.7	-2.4	-3.0	-3.6	-7.3	-14.9	-36.3	8.2	9.7
	PW91	-3.9	-3.5	-4.1	-4.8	-8.7	-16.9	-38.9	6.6	8.2
	RPBE	2.5	1.8	1.2	0.9	1.6	-4.4	-21.1	15.7	18.1
	BLYP	2.8	1.8	1.2	0.3	0.8	-7.4	-23.3	14.8	16.9
meta-GGA	TPSS	-0.1	-0.5	-1.1	-1.5	-4.9	-12.4	-35.3	10.2	11.4
	M06-L	-7.7	-5.3	-7.1	-8.2	-16.4	-27.8	-52.0	0.4	1.5
hybrid	PBE0	-3.0	-3.1	-4.0	-5.2	-9.9	-21.8	-46.9	4.8	5.1
	B3LYP	0.3	-0.4	-1.4	-2.8	-4.2	-16.2	-36.2	9.5	10.5
	M05-2X	-8.2	-6.6	-8.0	-10.8	-17.8	-36.3	-66.5	-3.8	5.6
	BHLYP	-2.1	-2.7	-4.1	-6.6	-9.6	-26.8	-51.1	3.5	3.8
long-range corrected	LC-BLYP	-6.2	-5.6	-7.0	-9.7	-15.1	-32.5	-60.3	-1.3	2.7
double-hybrid	B2PLYP	-3.1	-2.4	-4.7	-6.3	-10.0	-22.8	-46.6	4.5	4.9
					dispersion-corrected DFT					
empirical	PBE-D3	-10.7	-7.6	-7.9	-7.8	-12.1	-21.4	-47.3	1.8	4.3
	BLYP-D3	-12.1	-8.4	-7.7	-6.9	-9.1	-20.4	-47.2	2.2	5.2
	TPSS-D3	-10.9	-7.6	-7.6	-7.0	-11.8	-21.5	-51.3	1.4	3.6
	PBE0-D3	-11.4	-8.5	-9.0	-9.4	-14.8	-28.2	-58.5	-1.8	2.5
	B3LYP-D3	-12.5	-9.1	-9.1	-9.0	-12.0	-26.3	-55.3	-0.9	2.8
	B2PLYP-D	-8.7	-5.6	-8.2	-9.9	-14.0	-27.5	-55.4	-0.3	0.7
non-local correlation	optPBE	-10.6	-5.6	-9.2	-10.9	-12.5	-22.2	-42.5	2.0	5.5
	optB86b	-9.1	-4.5	-7.7	-9.0	-12.9	-22.3	-46.3	2.2	4.0
	vdW-DF2	-8.1	-4.6	-7.3	-8.9	-9.6	-19.1	-35.0	5.0	8.5
	vdW-DF1	-8.3	-3.8	-7.5	-9.1	-7.5	-16.5	-32.3	6.0	10.0
					wavefunciton-based methods					
MP2		-7.5	-4.8	-9.0	-10.3	-17.1	-30.7	-59.7	-1.7	2.3
CCSD(T)		-7.5	-4.8	-7.6	-9.8	-14.7	-27.7	-55.2	0.0	0.0
Color Scheme		-15.0	-5.0	0.0	5.0	15.0	25.0	35.0		

[a]The color scheme indicates the error (in kJ mol^{-1}) of each functional (red, underestimated interaction energy; blue, overestimated interaction energy) with respect to CCSD(T)/CBS reference calculations. All interaction energies calculated at the PBE/AVTZ geometry. [b]Mean signed error. [c]Root-mean-square deviation.

Cu(HCOO)$_2$ and Cu$_2$(HCOO)$_4$ cluster models. The interaction energies of water with a larger Cu$_2$(COO)$_4$ cluster model are reported for two distances between water and Cu^{2+}; R_{w-Cu} = 2.52 Å optimized for the H$_2$O···Cu(HCOO)$_2$ cluster model and R_{w-Cu} = 2.31 Å obtained at the PBE/AVTZ level for the H$_2$O···Cu$_2$(HCOO)$_4$ model (reported in parentheses in Table 3). Considering the former case, the error of none of the functionals investigated changes by more than 3 kJ mol^{-1}, going from a smaller to a larger cluster model. However, the transferability of the error of the DFT interaction energies between Cu(HCOO)$_2$ and Cu$_2$(HCOO)$_4$ cluster models becomes much worse when the R_{w-Cu} = 2.31 Å distance optimized for the larger cluster is considered; the errors associated with the transferability are larger than 4 kJ mol^{-1} in all the cases reported in Table 3 except for MP2, LC-BLYP and DFT/CC methods. Clearly, the DFT error depends on the distance between an adsorbate and an adsorbent.

Figure 2. Errors in the interaction energies of adsorbate−Cu(HCOO)$_2$ calculated with respect to the CCSD(T)/CBS level of theory. DFT functionals without and with explicit dispersion correction are shown in panels a and b, respectively.

Periodic-Model Calculations. While adsorption on small cluster models enables the benchmarking of the computationally convenient DFT-based approaches against highly accurate methods, the transferability of these results for the full periodic model needs to be tested. Moreover, the relative interaction energies for the CUS and other adsorption sites in MOFs should be carefully examined. Three important adsorption sites exist in the case of CuBTC: CUS, WIN, and CTR sites (Figure 1d). Since the CUSs are exposed to the main cage of the CuBTC structure, the interaction with organic linkers is relatively unimportant. On the contrary, in the case of the WIN and CTR sites, the interaction with organic linkers driven by dispersion plays a dominant role.

A proper choice of the reference method to evaluate the performance of different functionals in the full periodic model is critical. The DFT/CC approach was selected here as a reference level of theory for periodic models for the following reasons: (i) in addition to the dispersion correction, it attempts to correct all the errors of the local functional within the pairwise atom−atom approximation;[30,52] (ii) the transferability of the DFT/CC correction with the increasing size of the model is rather good (Table 3), which indicates that DFT error associated with wrong charge distributions on Cu^{2+} and organic linkers do not change its character with increasing model size and that those DFT errors can be represented to a large extent within pairwise approximation; and (iii) it has been shown in several studies that the DFT/CC approach yields the results in excellent agreement with the corresponding experimental data.[12,13,15,20] Note that the RMSD of DFT/CC for the data reported in Tables 1−2 is zero (the corresponding cluster models are part of the DFT/CC reference set by definition).

The interaction energies of CH$_4$, CO$_2$, propane, and propylene with CuBTC are summarized in Table 4, and the corresponding errors are given in Figure 3. In line with the observation made for the cluster model, the PBE functional strongly underestimates the interaction energies for all the adsorbates and adsorption sites studied. Quite surprisingly, LDA provides reasonably accurate results (RMSD = 5.8 kJ mol^{-1}), outperforming PBE and the nonlocal functionals investigated. However, it systematically overestimates the interaction energy on the CUS and WIN sites, while systematically underestimating the interaction with the CTR sites. The performance of nonlocal functionals is disappointing; none of the tested functionals (optPBE, optB86b, vdW-DF1, and vdW-DF2) can be recommended. All of these functionals gave relatively good interaction energies for CO$_2$

Table 2. Interaction Energies (in kJ mol^{-1}) of the Fe(HCOO)$_2$OH Cluster Model with CO$_2$ and CH$_4$ Molecules Calculated with Various Functionals^a

method	CO$_2$	CH$_4$
PBE	−12.0	−6.4
PBE-D3	−18.2	−16.9
M06-L	−29.5	−22.4
B3LYP	−16.9	−2.8
B3LYP-D3	−27.8	−19.2
M05-2X	−42.5	−28.1
LC-BLYP	−39.1	−19.7
B2LYP-D	−39.9	−14.1
optB86b	−25.5	−18.0
vdW-DF2	−20.7	−10.3
MP2	−40.4	−23.5
CCSD(T)	−34.6	−20.5

^{a}All interaction energies calculated at the CCSD(T)/CBS geometry.

Table 3. Error in the Interaction Energies (in kJ mol^{-1}) of Water With Cu(HCOO)$_2$ and Cu$_2$(HCOO)$_4$ Cluster Models with Respect to CCSD(T)/CBS Results^a

	DFT error			DFT error	
method	Cu(HCOO)$_2$	Cu$_2$(HCOO)$_4$	method	Cu(HCOO)$_2$	Cu$_2$(HCOO)$_4$
PBE	13	14 (19)	PBE-D3	6	8 (11)
TPSS	15	16 (21)	TPSS-D3	6	8 (11)
B3LYP	12	12 (16)	B3LYP-D3	1	3 (5)
M06-L	0	3 (4)	LC-BLYP	−5	−2 (−4)
B2LYP	5	6 (9)	B2LYP-D	0	2 (4)
vdW-DF2	9	12 (20)	MP2	−3	−3 (−4)
			DFT/CC	0	−1 (−1)

^{a}The CCSD(T)/CBS interaction energies of water with Cu(HCOO)$_2$ and Cu$_2$(HCOO)$_4$ clusters are −27.7 and −42.4 (−51.2) kJ mol^{-1}, respectively. Calculations on H$_2$O···Cu(HCOO)$_2$ performed at the PBE/AVTZ geometry; calculations of H$_2$O···Cu$_2$(HCOO)$_4$ performed at the PBE/AVTZ geometry with the r_{Cu-O} distance taken from H$_2$O···Cu(HCOO)$_2$ and from H$_2$O···Cu$_2$(HCOO)$_4$ (in parentheses).

Table 4. Interaction Energies (in kJ mol^{-1}) of CH$_4$, CO$_2$, Propane, and Propene with CuBTC; the Adsorption at the CUS, the WIN, and CTR Sites Was Considered (Figure 1d)^a

method	CH$_4$			CO$_2$			propane			propene		
	CUS	WIN	CTR	CUS	WIN	CTR	CUS	WIN	CTR	CUS	WIN	CTR
UFF	−1	−18	−22	−18	−25	−25	−13	−34	−52	28	−37	−46
LDA	−25	−25	−11	−34	−23	−19	−31	−38	−41	−69	−36	−41
PBE	−3	−2	2	−7	−3	2	−3	4	2	−25	8	−1
PBE-D2	−18	−24	−18	−21	−25	−21	−26	−41	−49	−58	−38	−46
PBE-D3	−16	−25	−19	−21	−26	−23	−26	−40	−52	−52	−36	−48
optPBE	−18	−36	−32	−29	−41	−41	−32	−59	−79	−62	−57	−74
optB86b	−19	−32	−27	−28	−36	−35	−32	−53	−72	−66	−53	−69
vdw-DF1	−11	−29	−28	−21	−35	−34	−23	−46	−66	−47	−44	−62
vdw-DF2	−11	−27	−23	−22	−30	−29	−20	−45	−59	−43	−43	−56
DFT/CC^b	−17	−21	−20	−28	−23	−23	−25	−33	−45	−60	−36	−46

^{a}The interaction energies were evaluated at DFT/CC equilibrium geometries. ^{b}Refs 12, 15, and 20.
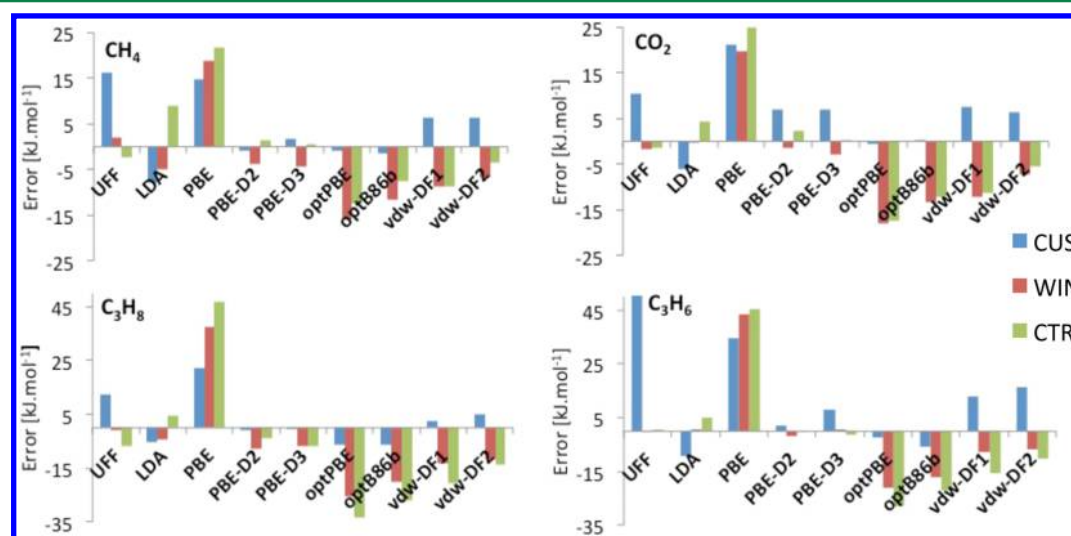
Figure 3. Errors in the interaction energies calculated for CH$_4$, CO$_2$, propane, and propene at CUS, WIN, and CTR sites with respect to the DFT/CC reference level of theory.

adsorption on the Cu(HCOO)$_2$ cluster model of the CUS. While optPBE and optB86b functionals give interaction energies with the CUS in the periodic model in good agreement with DFT/CC, vdW-DF1 and vdW-DF2 both fail to describe this interaction. In the case of CH$_4$ adsorption, both vdW-DF1 and vdW-DF2 significantly underestimate the adsorption on the CUS within the periodic model, while they provide an accurate description of the corresponding system within the cluster model. On the contrary, optPBE and optB86b functionals provide good interaction energies of CH$_4$ with the CUS within the periodic model despite the fact that these functionals overestimate this interaction within the cluster model by 20−30%. The large RMSD of optPBE and optB86b functionals (18.4 and 14.4 kJ mol^{-1}) evaluated for four adsorbates on three site types (the total of 12 adsorption complexes) is mostly caused by a strong overestimation of the adsorption on CTR sites. The slightly lower RMSD of vdW-DF1 and vdW-DF2 (11.5 and 9.1 kJ mol^{-1}) is misleading; both of these functionals overestimate the adsorption on the WIN and CTR sites, while the adsorption on the CUS is underestimated. It follows that all of the nonlocal functionals tested can provide unrealistic relative energies of individual adsorption sites (with propene being the most critical example).

An addition of semiempirical dispersion correction to the PBE (either D2 or D3) results in a significant improvement of the

calculated interaction energies with respect to the PBE, reaching actually the best overall RMSD values of 3.6 and 4.4 kJ mol^{-1} for PBE-D2 and PBE-D3, respectively. Although in most cases the error of both DFT-D2 and DFT-D3 is smaller than 4 kJ mol^{-1}, there are adsorption complexes whose interaction energy is either 7 kJ mol^{-1} underestimated (CO$_2$ on CUS) or 8 kJ mol^{-1} overestimated (propane on the WIN site).

Since MOFs are extensively studied using various empirical force-fields, UFF in particular, its performance was also evaluated. Surprisingly, the performance of UFF for WIN and CTR sites is superior to any DFT-based approach investigated herein, being (with the exception of propane adsorption at the cage-center site) in error by <2 kJ mol^{-1} with respect to the DFT/CC values. However, a complete failure of UFF to describe the adsorption at the CUS (underestimating more than 10 kJ mol^{-1}, Table 4) is not surprising.[11,15]

■ DISCUSSION

The interaction of various small molecules on Cu^{2+} and Fe^{3+} sites in MOFs was investigated with the cluster and periodic models at various levels of theory; the accuracy of different exchange−correlation functionals can be discussed based on the relatively large set of results presented above (Tables 1−4 and Figures 2 and 3). The transferability of the conclusions relevant to the

accuracy of the methods is of major interest. The method found suitable for an accurate description of a particular pair of adsorbate/adsorbent is often recommended for general use in the investigation of adsorption in MOFs,[18,19,21,26,62] but the transferability is not guaranteed. The following transferability issues are addressed: (i) the accuracy dependence on the adsorbate; (ii) the accuracy dependence on the size and geometry of the model; and (iii) the accuracy dependence on the adsorbent (different transition-metal cations in particular).

The molecules considered in the investigation with cluster models can be classified based on the type of the interaction with the CUS: (i) the dispersion-driven interaction (CH_4), (ii) the electrostatic and dispersion interactions (H_2, N_2, and CO_2), and (iii) the interaction with a partially covalent (dative) bonding character (CO, H_2O, and NH_3). The interaction energies calculated at the CCSD(T)/CBS level increase in the order H_2 < CH_4 < N_2 < CO_2 < CO < H_2O < NH_3. Note that also the error of density functionals increases in the same order (with a few exceptions). The accuracy of various types of exchange–correlation functionals decreases in the order B2PLYP-D < M06-L < LC-BLYP ~ hybrid with dispersion correction < GGA with dispersion correction ~ double hybrid < M05-2X ~ LDA < nonlocal functionals < hybrid < GGA. The B2PLYP-D functional (RMSD = 0.7 kJ mol^{-1}) can consistently and accurately describe the interaction of the $Cu(HCOO)_2$ cluster model with all the molecules investigated. The M06-L functional also gives rather accurate results (RMSD = 1.5 kJ mol^{-1}), and it can be used for the description of all the molecules investigated. The LC-BLYP describes very accurately the interaction of the molecules driven by dispersion and electrostatic forces; however, the interaction with H_2O and NH_3 is about 5 kJ mol^{-1} overestimated (RMSD = 2.7 kJ mol^{-1}). A similar observation can be made for nonlocal exchange–correlation functionals, which describe rather accurately the interaction driven by dispersion and/or electrostatic forces, whereas the adsorption complexes forming a partial dative bond (NH_3 in particular) are described very poorly.

The accuracy of exchange–correlation functionals depends also on the choice of the cluster model (Table 3). The error of all functionals depends on both the change of the cluster model (different pyramidalization on Cu^{2+}) and on the adsorbate–adsorbent distance, with the exception of the DFT/CC method. The DFT/CC approach provides a consistent description for potential energy curves, as shown previously.[12,13,30]

The transferability of accuracy for different adsorbents (Cu^{2+} vs Fe^{3+} CUS) is rather poor. While the interaction of CH_4 with the $Fe^{3+}(HCOO)_2(OH)$ cluster is well described at the M06-L, B3LYP-D3, and LC-BLYP levels, the interaction of CO_2 with this system described at the DFT level deviates by at least 5 kJ mol^{-1} with respect to reference CCSD(T)/CBS calculations. The most notable failure is that of the B2LYP-D functional (evaluated as the best functional in the case of Cu^{2+} systems), which overestimates the interaction of the $Fe^{3+}(HCOO)_2(OH)$ cluster with CO_2 by 5 kJ mol^{-1} and underestimates the one with CH_4 by 6 kJ mol^{-1}. While the interaction of CO_2 and CH_4 at the CCSD(T)/CBS level is −35 and −21 kJ mol^{-1}, respectively, it is −40 and −14 kJ mol^{-1}, respectively, at the B2LYP-D level. The calculations at the B2LYP-D level could thus lead to rather unrealistic relative interaction energies of different adsorbates in the case of Fe^{3+} CUSs. The results discussed above indicate that the best overall performance is found for M06-L and LC-BLYP functionals, which describe the interaction between various pairs of adsorbates and adsorbents most consistently. Nevertheless, an

error of at least 5 kJ mol^{-1} should be anticipated in the CUS-adsorbate interaction.

The results reported in Tables 1 and 4 show that the conclusions about the accuracy of exchange–correlation functionals based on cluster-model investigation are not necessarily transferable to a periodic model (the adsorption of CH_4 and CO_2). Calculations based on the periodic model show that the PBE-D2 and PBE-D3 level describes the interaction of CO_2 and hydrocabons with the CuBTC MOF relatively well; however, the problems with the description of the CUS are apparent. It must be pointed out that more problems must be anticipated for the description of the adsorbates forming a partial dative bond with the CUS. A failure of PBE-D2 and PBE-D3 to properly describe the water adsorption in CuBTC was reported[30] (with an error of over 10 kJ mol^{-1}), and those results are consistent with the cluster-model results reported in Table 1. The inability of the majority of DFT methods to describe the interaction of adsorbates with the CUSs properly together with the overestimated dispersion-driven interaction with small cages/windows results in a qualitatively incorrect description of the adsorption in MOFs. Such a qualitative failure is shown for CO_2 (all nonlocal functionals and dispersion-corrected functionals) and propene (all nonlocal functionals) in Table 4.

The performance of the UFF force field is surprisingly good for the adsorption sites, where the dominant interaction is dispersion (Table 4). However, the adsorbate–CUS interaction is described poorly with UFF, and thus new or additional force-field parameters are required. Computationally affordable MP2 provides worse results than some of the DFT functionals. Consequently, reliable force-field parameters can only be obtained upon a careful selection of the reference method suitable for a particular adsorbate–adsorbent interaction.[24]

The accuracy of various exchange–correlation functionals for the description of adsorption in MOFs has already been evaluated;[21,25−27] the relevant studies are briefly discussed below. One of the most recent studies performed by Toda et al.[21] for water interacting with a PDWL cluster model led to the following conclusions: (i) the best performing functionals were B2LYP-D and M05-2X functionals; and (ii) the best compromise between accuracy and computational feasibility was obtained for LC-BLYP and M06-L functionals. These conclusions are consistent with our results except for the performance of the M05-2X functional, which is caused by a different choice of the reference level of theory (CCSD(T)/CBS vs MP2/CBS). It is also noteworthy that the MP2/CBS level of theory used by Toda et al.[21] for the evaluation of the accuracy of functionals is not sufficiently accurate on its own (the RMSD of 2.3 kJ mol^{-1} for adsorbate/$Cu(HCOO)_2$ complexes), for complexes with non-negligible covalent bonding in particular. The discrepancy is even larger for the PDWL cluster; MP2/CBS was shown to overestimate strongly (by 5−8 kJ mol^{-1}) the interaction with H_2O, ethylene, and CO molecules with respect to the CCSD(T)/CBS level.[12,13,30] The interaction of a large set of small molecules (containing H_2O, N_2 and NH_3 molecules among others) with CUSs has recently been studied by Supronowicz et al.,[27] who employed both PDWL and enlarged cluster models (dicopper tetrabenzenetricarboxylate, Cu_2BTC_4); however, they considered only the B3LYP-D3 functional.

The efficiency and reliability of the methods for the description of the interaction of small molecules with CUSs were also evaluated in two studies by Rana et al.,[26,63] who studied the adsorption of CO_2 in CuBTC and M-DOBDC (M = Mg, Ni, and Co) MOFs. Based on a comparison with the averaged

experimental data available, it was concluded that the vdW-DF1 functional was an optimal choice for the description of CO_2 interaction with MOFs containing alkaline-earth or transition-metal CUSs. This conclusion is in sharp contrast with the results reported herein for CO_2 adsorption in CuBTC; all of the nonlocal exchange−correlation functionals considered predict preferential CO_2 adsorption at WIN and CTR sites, contrary to experimental results[7] and DFT/CC investigation[20] (Table 4). Thus, the conclusions drawn for CuBTC in ref 26 are only fortuitously in agreement with experimental data due to the fact that the interaction with WIN and CTR sites was not considered. It is apparent that the investigation of the adsorption on only one type of adsorption site can lead to wrong conclusions and recommendations.

CONCLUSIONS

The accuracy of exchange−correlation functionals for the description of adsorption in MOFs was evaluated with respect to the CCSD(T)/CBS level of theory (cluster models) and with respect to DFT/CC and experimental data (periodic models). No general recommendation valid for all adsorbate/MOF systems can be given. The accuracy of individual functionals depends on a particular adsorbate and adsorbent and even on the model size and geometry.

The highest accuracy for the Cu^{2+} cluster model was found for B2PLYP-D, but this functional fails to describe the interaction with the Fe^{3+} cluster model. The calculations employing cluster models (both Cu^{2+} and Fe^{3+}) indicate that the most concise results with respect to the CCSD(T)/CBS reference level of theory are obtained with M06-L and LC-BLYP functionals; nevertheless, errors of up to 5 kJ mol^{-1} can be observed in the case of the Fe^{3+} CUS. Unfortunately, none of these functionals can be routinely employed for calculations employing the periodic model. Evaluation of the exact exchange required for LC-BLYP makes the calculations on periodic models computationally prohibitive; in addition, the LC-BLYP cannot be expected to accurately describe adsorption sites, where the dispersion interaction with organic linkers starts to play a dominant role (e.g., cage-center or cage-window sites). Calculations employing the meta-GGA M06-L functional are also more expensive for periodic models, and a serious SCF convergence problem has been encountered, preventing us from reporting any results with the periodic model and M06-L functional. Consequently, the performance of M06-L for WIN and CTR sites has not been evaluated.

Among the functionals tested on the periodic model of CuBTC with respect to DFT/CC and experimental data, the GGA functionals augmented with semiempirical correction for the dispersion (D2 and D3) perform the best, showing reasonable accuracy with RMSD values of 3.6 and 4.4 kJ mol^{-1} for PBE-D2 and PBE-D3, respectively. Note, however, that the accuracy of GGA+D methods depends significantly on the adsorbate orientation and distance from the MOF framework and that the errors found for the CUS often have the opposite sign from those found for dispersion-stabilized adsorption sites (WIN and CTR). This may result in a qualitatively wrong order of interaction energies at various adsorption sites (propene and CO_2) and an incorrect adsorption mechanism (CH_4 adsorption in CuBTC).[15] The results reported herein for cluster models indicate that the replacement of the GGA with hybrid or even double-hybrid functionals improves the description of the system, but a sharp increase of computational expenses makes such calculations for periodic models prohibitively expensive.

The overall performance of the nonlocal functionals investigated is insufficient, and they cannot be recommended for general use. The main problem is a wrong description of the relative stabilities of different adsorption sites in CuBTC. All of the investigated nonlocal functionals tend to overestimate strongly the interaction energy for dispersion-stabilized sites.

The rather disappointing performance of exchange−correlation functionals evaluated here for the description of adsorption in MOFs containing CUSs leads us to the following conclusions: (i) none of the functionals can be recommended for general use for MOFs; (ii) a suitable functional should be selected for a particular system based on a comparison with carefully selected benchmark data always considering adsorption at all relevant site types for the material concerned; and (iii) conclusions about the method accuracy are not transferable to other systems. Therefore, the most practical and accurate approach is to find a suitable semilocal GGA functional and add the correction term for the dispersion. The reparameterization of dispersion correction may be required for interaction with the CUSs in particular; in such a case, the error of DFT for the interaction with the transition metal can be effectively corrected. The most accurate results can be obtained with the correction schemes such as DFT/CC, which, by definition, does not merely add the dispersion term; instead, it attempts to fix the overall DFT error, including missing dispersion.

ASSOCIATED CONTENT

ⓈSupporting Information
The CASPT2 calculations on model cluster containing Fe^{3+} are given along with more detailed analysis of DFT functionals performance. The cluster/adsorbate geometries are also reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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