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Authors

Witte, Jonathon
Neaton, Jeffrey B
Head-Gordon, Martin

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Assessing electronic structure approaches for gas-ligand interactions in metal-organic frameworks: the CO₂-benzene complex

Jonathon Witte,^{1,2} Jeffrey B. Neaton,^{2,3, a)} and Martin Head-Gordon^{4, 5, b)}

¹⁾*Department of Chemistry, University of California, Berkeley, California 94720, USA*

²⁾*Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

³⁾*Department of Physics, University of California, Berkeley, CA 94720, USA*

⁴⁾*Department of Chemistry, University of California, Berkeley, CA 94720, USA*

⁵⁾*Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

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Adsorption of gas molecules in metal-organic frameworks is governed by many factors, the most dominant of which are the interaction of the gas with open metal sites, and the interaction of the gas with the ligands. Herein, we examine the latter class of interaction in the context of CO₂ binding to benzene. We begin by clarifying the geometry of the CO₂-benzene complex. We then generate a benchmark binding curve using a coupled-cluster approach with single, double, and perturbative triple excitations [CCSD(T)] at the complete basis set (CBS) limit. Against this Δ CCSD(T)/CBS standard, we evaluate a plethora of electronic structure approximations: Hartree-Fock, second-order Møller-Plesset perturbation theory (MP2) with the resolution-of-the-identity approximation, attenuated MP2, and a number of density functionals with and without different empirical and nonempirical van der Waals corrections. We find that finite-basis MP2 significantly overbinds the complex. On the other hand, even the simplest empirical correction to standard density functionals is sufficient to bring the binding energies to well within 1 kJ/mol of the benchmark, corresponding to an error of less than 10%; PBE-D in particular performs well. Methods that explicitly include nonlocal correlation kernels, such as VV10, vdW-DF2, and ω B97X-V, perform with similar accuracy for this system, as do ω B97X and M06-L.

^{a)}Electronic mail: jboneaton@lbl.gov

^{b)}Electronic mail: mhg@cchem.berkeley.edu

I. INTRODUCTION

Metal-organic frameworks (MOFs) constitute a promising class of materials for CO₂ separation.¹ MOFs are three-dimensional nanoporous solids consisting of metal centers connected by organic ligands; there exist a tremendous number of synthetically accessible combinations of ligands and metals.² Extensive studies have been conducted to determine the impact of changing the metal center on CO₂ adsorption,^{3–7} but there is a relative paucity of work emphasizing the contribution of the ligand.⁸ Although open metal sites are commonly regarded as the most thermodynamically favorable binding locations for gas molecules, the ligands themselves also contribute significantly to adsorption, and are hence worthy of further investigation.^{8,9}

A handful of studies have involved the investigation of the binding of CO₂ to various forms of organic linkers, predominantly functionalized variants of benzene,^{10–13} but to date only one study has considered the interaction at nonequilibrium distances.¹⁴ These nonequilibrium distances are particularly relevant in the context of CO₂ uptake in MOFs. Additionally, no studies have systematically evaluated the ability of the various existing electronic structure approximations to describe this gas-ligand interaction. The existing literature has established density functional theory (DFT) as the primary workhorse for such systems, a consequence of its ability to balance computational cost [typically $O(N^3)$] with accuracy.^{15,16} However, the famed Jacob’s ladder of DFT does not offer a clear way to systematically improve results.¹⁷ Moreover, the local nature of DFT within standard approximations renders it incapable of describing long-range London dispersion, an integral component of noncovalent interactions such as gas-ligand binding.¹⁸ To account for this, a number of dispersion corrections to standard density functional theories have been developed: the DFT-D, DFT-D2, and DFT-D3 approaches of Grimme,^{19–21} the exchange-hole dipole moment (XDM6 and XDM10) model of Becke and Johnson,^{22–28} and methods incorporating fully nonlocal correlation kernels.^{29–32} For an overview of these methods (and many more), the reader is referred to a recent review by Klimeš and Michaelides.³³ This additional “stairway” of dispersion corrections further complicates the DFT picture. Although efforts are underway to develop generally-applicable functionals, it is often not clear *a priori* what the best functional for a particular application is.

In stark contrast, the hierarchy of wavefunction-based (WF) methods offers a clear path

to systematically obtaining more accurate energies, but at much steeper costs: even the simplest method of incorporating electronic correlation in WF theory, second-order Møller-Plesset perturbation theory (MP2), scales as $O(N^5)$, and methods that incorporate higher-order correlation effects, such as coupled-cluster theory with single, double, and perturbative triple excitations [CCSD(T)], suffer from even worse scaling. Even MP2 can be prohibitively expensive for calculations involving extended systems. The resolution-of-the-identity (RI) approximation partly addresses this cost by reducing the prefactor of the calculation, but the underlying scaling is left unchanged.^{34–37} Additionally, MP2 performs quite poorly for certain classes of systems (notably those involving aromatic interactions) and converges quite slowly with respect to the size of the basis set.^{38,39} Attenuation of the Coulomb operator (attenuated MP2) attempts to address some of these problems (as well as that of basis set superposition error, or BSSE), with the added benefit of introducing sparsity that could be exploited to potentially reduce scaling.^{40,41}

In this work, we evaluate a multitude of electronic structure approximations for the CO₂-benzene complex, a well-defined model system that is also a simple model of a gas binding to a nonfunctionalized organic linker. We begin by elucidating the equilibrium geometry of the complex, since there are conflicting reports in the literature.^{12,13,42} We then characterize the CO₂-benzene potential energy surface using a wide variety of methods, assessing their strengths and weaknesses. We find MP2 significantly overbinds the complex, particularly in a finite basis, and hence is unsuitable as a benchmark in dispersion-bound systems. We also find standard semilocal density functionals are – with some notable exceptions – generally inadequate for this particular system, although this deficiency is rectifiable via the addition of a simple C_6 dispersion correction or an explicitly nonlocal correlation kernel.

II. COMPUTATIONAL METHODS

Throughout this study, all MP2 calculations employed the RI approximation, but the RI prefix has been omitted. For all geometry optimizations, we utilized the dual-basis approximation to HF in conjunction with MP2 (DB-MP2),^{43–45} with basis set pairings from Steele et al.⁴⁶ We feel this approximation is justified based on the high degree of accuracy it has demonstrated in previous studies,^{46,47} as well as in this particular study (see supplemental material).⁸⁹

A series of geometry optimizations were performed for the various possible symmetries (C_{2v} , C_s , and C_1) of the flat-on conformations of the benzene- CO_2 system at the DB-MP2 level with the dual-basis pairing for Dunning’s augmented correlation-consistent polarized valence double-zeta basis (aug-cc-pVDZ).^{46,48,49} The Hessians and geometries for these calculations were then utilized as initial guesses in subsequent geometry optimizations at the DB-MP2 level with the dual-basis pairing for the larger aug-cc-pVTZ basis. Single point energy calculations were performed at the same level of theory for each structure in the aug-cc-pVQZ basis, then extrapolated to the basis set limit using the two-point ($T \rightarrow Q$) formula of Helgaker.³⁹ The conformation exhibiting the lowest energy at the extrapolated CBS limit was determined to be the optimal structure and was utilized in subsequent benchmarking.

In order to evaluate various methods, a series of one-dimensional potential energy surfaces of the benzene- CO_2 system were generated. The intermolecular structural parameter for these binding curves was the projected distance between the carbon atom in CO_2 and the ring center of benzene onto the principal axis of benzene. A wide variety of electronic structure methods were considered in the aug-cc-pVTZ basis: MP2,^{50,51} attenuated MP2,^{40,41} CCSD(T),⁵² B3LYP,^{53–56} B97,⁵⁷ B97-D,²⁰ PBE,⁵⁸ PBE0,⁵⁹ TPSS,⁶⁰ TPSSh,⁶¹ M06-L,⁶² M06-2X,⁶³ M11,⁶⁴ ω B97X,⁶⁵ ω B97X-D,⁶⁶ ω B97X-V,⁶⁷ vdW-DF2 (rPW86+PW92),^{32,58,68} VV10 (rPW86+PBE),^{30,68,69} XDM6 (PW86+PBE),^{22,23,58,70} and Grimme -D2 and -D3 corrections to some of the standard GGA functionals.^{20,71} The MP2 correlation energy was extrapolated to the basis set limit ($T \rightarrow Q$),³⁹ and a frozen-core (fc) CCSD(T) correction to the MP2/CBS correlation energy was calculated in the cc-pVTZ basis as:⁷²

$$E_{\Delta\text{CCSD(T)}}^{\text{CBS}} = E_{\text{MP2}}^{\text{CBS}} + (E_{\text{CCSD(T) (fc)}} - E_{\text{MP2 (fc)}})^{\text{TZ}}. \quad (1)$$

This benchmark was calculated both with and without the counterpoise correction (CP) for basis set superposition error (BSSE),⁷³ and the region bounded by the two curves, denoted $\Delta\text{CCSD(T)}/\text{CBS}$, represents the standard against which all other methods are evaluated. With the exception of this benchmark curve, all other results reported herein do not employ any form of counterpoise correction. Such corrections are expensive and the ideal method should not necessitate them; furthermore, in the aug-cc-pVTZ basis, these corrections are typically very small for density functionals, a consequence of the relatively fast convergence of most density functionals with respect to basis set size.⁷⁴ For purposes of comparison, however, counterpoise-corrected results for almost all methods are provided in the supplemental

material.⁸⁹

A fine Lebedev integration grid consisting of 75 radial points and 302 angular points was utilized in the computation of the exchange-correlation components of all of the density functionals. With the exception of CCSD(T) and MP2, all calculations were performed in the aug-cc-pVTZ basis. Moreover, for the RI calculations, the auxiliary basis sets of Weigend were used.⁷⁵ For all calculations, integral thresholds of 10^{-14} a.u. were used, and no symmetry was exploited, save the symmetry of the system itself during all geometry optimizations. All calculations were performed with a development version of Q-Chem 4.1.⁷⁶ Molecular structures were generated with Avogadro.⁷⁷

III. RESULTS AND DISCUSSION

A. Geometry

In this study, the geometry of the benzene-CO₂ system was optimized at the DB-MP2 level in the dual-basis pairing for aug-cc-pVTZ. The optimized geometry of the benzene-CO₂ dimer is provided in Figure 1. The optimal dimer geometry, unlike that reported by Mackie and DiLabio,¹² is C_s-symmetric, with the principal axis of CO₂ bisecting a carbon-carbon bond of benzene. The CO₂ molecule exhibits a slight deviation from linearity and is not strictly parallel to the benzene ring. These findings compare favorably with related studies by Besnard *et al.*⁴² and Chen *et al.*¹³

There exists a small (1 kJ/mol) thermodynamic driving force to break C_{2v} symmetry, but the potential energy surface appears to be largely invariant to rotation of the CO₂ about the principal axis of benzene, as evidenced by calculations involving the atom-centric C_s structure (see supplemental material).⁸⁹

B. Binding Curves

In order to assess the ability of various electronic structure methods to describe the interaction between benzene and CO₂, the optimized structure of CO₂ was rigidly translated along the principal axis of benzene. Twelve distinct intermolecular separations were thus sampled, where the intermolecular separation has been defined as the projection onto the principal axis of benzene of the distance between the carbon atom of CO₂ and the center of

FIG. 1. Calculated equilibrium structure of the benzene-CO₂ system, determined at the DB-MP2 level of theory with the dual-basis pairing for Dunning’s augmented correlation-consistent polarized valence triple-zeta basis. The complex possesses C_s symmetry.

the ring. The resulting potential energy surfaces are portrayed in Figures 2-7.

We begin our analysis with the standard wavefunction-based methods, with results summarized in Figure 2. The region bounded by the counterpoise-corrected (CP) and noCP Δ CCSD(T)/CBS curves represents our best guess of the true potential energy surface along this coordinate and the uncertainty associated therewith. The equilibrium intermolecular separation at this level of theory is found to be 3.25 ± 0.01 Å, corresponding to a binding energy on the order of 10.2 ± 0.4 kJ/mol. It is worth noting that, contrary to expectations, the CP curve actually lies below the noCP curve, which may be indicative of the limitations of extrapolation to the CBS limit.

Relative to the Δ CCSD(T)/CBS benchmark, Hartree-Fock theory (HF) provides a rather poor description of the potential energy surface; this is unsurprising, given the lack of correlation beyond Pauli exclusion in HF. However, HF theory does yield a bound complex, with a binding energy curve whose asymptotic form scales with the inverse fifth power of intermolecular distance. This is consistent with expectations: both CO₂ and benzene are known to be characterized by significant quadrupole moments.

The addition of MP2 correlation significantly improves the description of the complex relative to HF. However, MP2 theory systematically predicts overbinding in this particular system, regardless of the choice of basis set. As the size of the basis set increases, so too does the quality of the description, but even at the extrapolated CBS (T $\rightarrow$ Q) limit, the minimum binding energy is in error by upwards of 15% relative to the benchmark Δ CCSD(T)/CBS

FIG. 2. Binding energy curves for the benzene- CO_2 complex obtained with various wavefunction-based methods. The region denoted $\Delta\text{CCSD(T)}/\text{CBS}$ is bounded by CP- and non-CP-corrected $\Delta\text{CCSD(T)}$ curves, and represents our best guess at the true binding curve. None of the other methods employ the CP correction. The inset is a close-up of the region around the equilibrium distance (note different scale), and the curves connecting the points are merely smooth fits to the data. The equilibrium intermolecular separations for each method (listed to the right of the legend as r_e) were determined by cubic spline interpolation of the data. The reported r_e for $\Delta\text{CCSD(T)}/\text{CBS}$ is the average of the $\Delta\text{CCSD(T)}/\text{CBS}$ noCP and CP equilibrium intermolecular separations. For ease of analysis, the legend has been ordered (with the exception of the benchmark $\Delta\text{CCSD(T)}/\text{CBS}$ region) to mirror the ordering of the binding curves near the equilibrium separation.

value. Moreover, the equilibrium separation of the benzene and CO_2 molecules is significantly smaller (on the order of $0.2 \text{ \AA}$) for finite-basis MP2 than for $\Delta\text{CCSD(T)}/\text{CBS}$, which is again indicative of overbinding. Fundamentally, this overbinding is attributable to the fact that the frequency-dependent polarizabilities (and hence C_6 coefficients, as per the Casimir-Polder relation) of MP2 are identical to those of uncoupled HF (UCHF) theory.⁷⁸

More specifically, the UCHF polarizabilities of benzene are likely the chief contributor to overbinding; the carbon dioxide dimer is well-described by MP2 theory, whereas the benzene dimer is known to be significantly overbound.^{38,79} It is clear from these results that MP2 is unsuitable as a benchmark for systems with significant dispersion interactions, even in the large aug-cc-pVQZ basis, and hence a more complete description of correlation is required.

Attenuation of the Coulomb operator in MP2 (attMP2 in Figure 2) addresses some of this overbinding. In fact, the attenuated MP2 method in the aug-cc-pVTZ basis performs similarly to standard MP2 in the much larger aug-cc-pVQZ basis, at least in the vicinity of the binding minimum. Unfortunately, this improvement comes at the expense of the description at larger intermolecular separations – the rate with which the attenuated MP2 interaction energy diminishes with separation is unphysical. Moreover, attenuated MP2 predicts a tighter equilibrium geometry of the complex than $\Delta\text{CCSD(T)}$. Despite these caveats, attenuated MP2 still represents a notable improvement over standard, finite-basis MP2 in this system.

In addition to the aforementioned wavefunction-based approaches, we have applied a number of density functionals of varying degrees of sophistication to this system. The simplest such functionals utilized here are of the GGA variety: PBE; the global hybrid GGAs PBE0, B97, and B3LYP; and the long-range corrected hybrid GGA ωB97X . As is evident from Figure 3, all of the GGA functionals employed, with the exception of ωB97X , produce qualitatively-incorrect binding energy curves that bear striking resemblance to the HF curve, and it is notable that all of these methods predict a bound complex. The strikingly-good performance of ωB97X could be, to some extent, a result of the incorporation of range-separated exchange, though it is more likely an artifact of training: unlike the other GGA functionals examined here, ωB97X was trained on noncovalent interactions.

Slightly more sophisticated than these GGA functionals are functionals of the meta-GGA variety. Here, we examined the empirical TPSS, its hybrid variant TPSSh, and a number of Minnesota functionals: the local M06-L, the global hybrid M06-2X, and the more recent range-separated hybrid M11. Binding curves obtained using these functionals are provided in Figure 4. We see that the empirical TPSS and TPSSh functionals suffer from similar issues as the GGA functionals: the kinetic energy density is not sufficiently nonlocal so as to capture dispersion interactions. The Minnesota functionals provide a much better description of the binding, though this is likely attributable to their high degrees of parametrization, as

FIG. 3. Binding energy curves for the benzene- CO_2 complex obtained with various standard, hybrid, and long-range corrected hybrid GGA functionals in the aug-cc-pVTZ basis with a (75,302) integration grid. For further details, see Figure 2.

well as the fact that their training sets included noncovalent interactions. Unfortunately, this improved description is not without its flaws: the Minnesota functionals, particularly M06-2X and M11, are hampered by incorrect asymptotics and unphysical oscillations in binding energy with increasing separation.^{80,81} M06-L is clearly the top performer amongst the meta-GGA functionals for this particular system, even outperforming MP2 at the basis set limit in the vicinity of the equilibrium binding distance.

The next degree of sophistication of DFT explored here constitutes a departure from Perdew’s ladder – we’ll henceforth be traversing the stairway of Klimeš and Michaelides.³³ The first such step we consider involves Grimme’s empirical DFT-D2 correction to GGA functionals (henceforth referred to, for simplicity, as DFT-D, since the original iteration of DFT-D is not in common use).²⁰ We consider -D corrections to B3LYP, PBE, and PBE0, and we also examine Grimme’s unhybridized B97-D, as well as $\omega\text{B97X-D}$. The binding energy curves associated with these methods are given in Figure 5. Comparing these results to

FIG. 4. Binding energy curves for the benzene- CO_2 complex obtained with various standard, hybrid, and range-separated hybrid meta-GGA functionals in the aug-cc-pVTZ basis with a (75,302) integration grid. For further details, see Figure 2.

those of Figure 3, we see that addition of even the simplest form of dispersion correction improves the description of binding in the benzene- CO_2 complex drastically. However, there is a caveat: the choice of damping function is quite important. PBE0-D exhibits significant overbinding near the equilibrium separation when the damping function associated with Grimme’s DFT-D is used; however, use of the damping function of Chai and Head-Gordon⁶⁶ (CHG) yields significantly better energetics near the equilibrium geometry, though at the cost of lethargic decay of the binding energy in the intermediately-stretched regime. See supplemental material and Figure 6 – the PBE0-D (CHG) and PBE0-D3 curves are very similar.⁸⁹ Among the DFT-D methods, PBE-D exhibits the best performance, only deviating from the benchmark curves at very compressed geometries, where the overly repulsive PBE exchange contribution dominates.

The next step of complexity in describing dispersion interactions involves factoring in the local environment to the standard C_6 correction. This encompasses the DFT-D3 correction

FIG. 5. Binding energy curves for the benzene- CO_2 complex obtained with various DFT-D2 methods in the aug-cc-pVTZ basis with a (75,302) integration grid. For further details, see Figure 2.

of Grimme, as well as the XDM model of Becke and Johnson.^{21,22} Binding energy curves for PBE-D3, PBE0-D3, and XDM6 (with PW86 exchange and PBE correlation) are provided in Figure 6. Comparing the PBE-D3 and PBE0-D3 curves to the DFT-D curves of Figure 5, we see that although accounting for the local environment introduces another layer of complexity, this additional complexity does not necessarily correspond to an improvement of the description – the -D3 methods exhibit curves which are shifted significantly (around 0.1 Å) towards larger intermolecular separations, with broader wells. Moreover, comparison with the PBE0-D (CHG) results (see supplemental material)⁸⁹ shows that perhaps the largest difference between the -D and -D3 methods is not actually this environmental dependence, but rather the choice of damping function: DFT-D3 utilizes the same form of damping function as -D (CHG).

The XDM approach, though also quite good here, comes with its own disclaimer: it is

highly sensitive to the choice of exchange and correlation functionals. A number of other xc functionals were examined in conjunction with both XDM6 and XDM10 (using parameters recommended by various authors), but the performances of most are unsatisfactory – for instance, the PW86+PBE+XDM10 approach, using optimized parameters from Becke et al.,²⁷ shifts the binding minimum to the right by roughly 0.4 Å and only recovers 25% of the equilibrium binding energy). These data may be found in the supplemental material.⁸⁹

FIG. 6. Binding energy curves for the benzene- CO_2 complex obtained with various methods employing environmentally-dependent C_6 corrections in the aug-cc-pVTZ basis with a (75,302) integration grid. For further details, see Figure 2.

The most sophisticated class of methods examined in this study explicitly incorporate nonlocal contributions to correlation: vdW-DF2, VV10, and $\omega\text{B97X-V}$. As illustrated in Figure 7, these methods describe the binding of CO_2 to benzene reasonably well through all intermolecular separations examined. All of the nonlocal methods overbind slightly at their respective equilibrium geometries, which is indicative of marginally inflated C_6 coefficients. The issues associated with exchange-matching in vdW-DF2 are manifest in fact that the entire vdW-DF2 curve appears to be shifted 0.1 Å to the right of the $\Delta\text{CCSD(T)}$ benchmark,

but other than this, none of the methods here deviate by much more than 1 kJ/mol except at the most compressed geometry, where the overly repulsive exchange components begin to dominate.

FIG. 7. Binding energy curves for the benzene- CO_2 complex obtained with various nonlocal methods in the aug-cc-pVTZ basis with a (75,302) integration grid. For further details, see Figure 2.

IV. CONCLUSION

In this work, we have clarified the geometry of the benzene- CO_2 complex and systematically generated a series of binding energy curves for the complex using a multitude of electronic structure approximations. More specifically, we have assessed the efficacy of HF, MP2, CCSD(T), and a number of DFT exchange-correlation functionals with and without different empirical and nonempirical van der Waals corrections with regard to the description of binding in the benzene- CO_2 complex.

We find that although HF predicts a bound complex – a consequence of a significant

quadrupole-quadrupole electrostatic interaction – the energetics and intermonomer distance predicted at such a low level of theory leave much to be desired; the inclusion of electronic correlation is necessary to achieve any semblance of quantitative accuracy. Moreover, this description of electronic correlation must be sufficiently nonlocal, as exemplified by the failure of conventional semi-local density functionals (e.g. PBE, TPSS) to correctly reproduce the $\Delta\text{CCSD(T)}$ binding energy curve. Some semi-empirical functionals, namely those in the Minnesota suite, perform quite well in the vicinity of the minimum, but they are hampered by incorrect asymptotics and unphysical oscillations. Standouts amongst the standard GGA and meta-GGA functionals are ωB97X and M06-L, which describe the binding quite well throughout a range of intermolecular separations; the exemplary performance of these functionals may be largely attributable to the inclusion of noncovalent interactions in their respective training sets.

The simplest wavefunction-based approach to correlation – MP2 theory – while qualitatively correct, yields substantial overbinding in finite basis sets, and overbinds noticeably even when extrapolated ($T \rightarrow Q$) to the CBS limit. Attenuation of the Coulomb operator addresses some of this overbinding and improves the performance of MP2 in the vicinity of the equilibrium separation, but at the cost of the long-range limit. In contrast, even the simplest density-functional-based method of treating dispersion, i.e. the addition of an empirical C_6 correction (DFT-D), is sufficient to bring standard GGA functionals within 1 kJ/mol of the $\Delta\text{CCSD(T)}$ benchmark, depending on the choice of damping function: PBE-D in particular performs quite well. Methods that explicitly address nonlocal correlation – VV10, vdW-DF2, and $\omega\text{B97X-V}$ – are also rather well-suited to this system, although vdW-DF2 predicts a characteristically too-large intermonomer distance, consistent with an overly-repulsive exchange component, and all of the nonlocal methods overbind slightly at their respective equilibrium separations.

The extent to which the impressive accuracies of the DFT-D, M06-L, $\omega\text{B97X-V}$, and VV10 methods are transferable to larger, more diverse systems – namely a variety of MOFs – remains to be seen. The vdW-DF2 method has been validated on a wide variety of systems, and its performance has been remarkably consistent.^{9,82–85} To date, VV10 has only been benchmarked on noncovalent interactions in systems containing small molecules; although the results have been promising – particularly when range-separated exchange is employed – the method has yet to be validated for larger systems, such as MOFs.^{84,86} On the other hand,

PBE-D has been demonstrated to be reasonably successful at predicting CO₂ adsorption energies in a few MOF variants,^{9,85} though the failure of PBE-D3 to describe H₂ binding to Cu surfaces again underscores the potential sensitivity of the -D brand of methods to the choice of damping function and C_6 coefficients.⁸³ M06-L has recently been applied, with some success, to hydrocarbon adsorption in Fe-MOF74.⁸⁷ The ω B97X-V functional is quite new, and although it has excelled in a wide variety of systems, the range-separated exchange component hinders its adaptation into periodic codes.⁶⁷ This is not necessarily a problem, as calculations on cluster models of MOFs have the potential to be quite accurate,^{87,88} but it is certainly a limitation of not only ω B97X-V, but also long-range corrected variants of VV10.

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