High-throughput screening of small-molecule adsorption in MOF

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Using high-throughput screening coupled with state-of-the-art van der Waals density functional theory, we investigate the adsorption properties of four important molecules, \(\text{H}_2\), \(\text{CO}_2\), \(\text{CH}_4\), and \(\text{H}_2\text{O}\) in MOF-74-\(M\) with \(M = \text{Be}, \text{Mg}, \text{Al}, \text{Ca}, \text{Sc}, \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Sr}, \text{Zr}, \text{Nb}, \text{Ru}, \text{Rh}, \text{Pd}, \text{La}, \text{W}, \text{Os}, \text{Ir}, \text{and} \text{Pt}\). We show that high-throughput techniques can aid in speeding up the development and refinement of effective materials for hydrogen storage, carbon capture, and gas separation. The exploration of the configurational adsorption space allows us to extract crucial information concerning, for example, the competition of water with \(\text{CO}_2\) for the adsorption “pockets.” We find that only a few noble metals—\text{Rh}, \text{Pd}, \text{Os}, \text{Ir}, and \text{Pt}—favor the adsorption of \(\text{CO}_2\) and hence are potential candidates for effective carbon-capture materials. Our findings further reveal significant differences in the binding characteristics of \(\text{H}_2\), \(\text{CO}_2\), \(\text{CH}_4\), and \(\text{H}_2\text{O}\) within the MOF structure, indicating that molecular blends can be successfully separated by these nano-porous materials.

I. INTRODUCTION

The modular building-block nature of metal organic framework (MOF) materials makes these hybrid systems very intriguing for a variety of technologically important applications, ranging from gas storage,1–9,10 and gas sequestration10–29 to more exotic applications.29 The extraordinary diversity demonstrated by MOFs derive primarily from their vast range of organic linkers combined with the wide chemistry of metal atoms (or clusters), which alter their responses to many external physical and chemical stimuli and influence their flexibility, affinity towards adsorbing molecules, and intrinsic reactivity. In this regard, much progress has been made improving the adsorption properties of MOFs. For example, MOFs with unsaturated metal centers such as MOF-74-\(M\) with \(M = \text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{and} \text{Zn}\) show improved adsorption densities for \(\text{H}_2\) and \(\text{CH}_4\) and faster adsorption at small partial \(\text{CO}_2\) pressures, the latter of which is highly desirable for \(\text{CO}_2\) capturing applications.30–33

Although considerable experimental effort has gone into the synthesis, characterization, and study of adsorption properties of target molecules in MOFs, such work typically requires a significant amount of time, slowing down scientific progress. Thus, the help of computational material science becomes crucial, accelerating and guiding the refinement of existing materials as well as the prediction of new MOFs. A very promising approach is the so-called high-throughput screening (HTS), which—in a much shorter time compared to experiment—screens many possible materials; it is well established in the fields of pharmacology and biology and just recently was introduced into the materials science community. Excellent examples of HTS are the materials project41–46 and the material genome initiative.47

In this work we demonstrate the importance of HTS to accelerate the discovery of MOFs with better adsorption properties for gas-storage and gas-separation applications. We focus on one particular MOF, i.e. MOF-74, because of its unprecedented adsorption characteristics and specificity towards \(\text{CO}_2\), which makes it very important for the process of separating \(\text{CO}_2\) from \(\text{CH}_4\) in low-quality gas such as biogas. We start with MOF-74-Zn and use HTS to study its large configurational adsorption space and element space. Specifically, we study the adsorption properties of four important molecules, i.e. \(\text{H}_2\), \(\text{CH}_4\), \(\text{CO}_2\), and \(\text{H}_2\text{O}\) in combination with 25 different metals, which are: \text{Be}, \text{Mg}, \text{Al}, \text{Ca}, \text{Sc}, \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Sr}, \text{Zr}, \text{Nb}, \text{Ru}, \text{Rh}, \text{Pd}, \text{La}, \text{W}, \text{Os}, \text{Ir}, \text{and} \text{Pt}. \) Interestingly, from this list only eight iso-structural MOF-74-\(M\) with \(M = \text{Ti}, \text{Mg}, \text{Mn}, \text{Ni}, \text{Co}, \text{Fe}, \text{Zn}, \text{and} \text{Cu}\) have been synthesized since 2005, attesting to the long experimental time-scale. The pioneering contribution of Park et al.48 in the study of \(\text{CO}_2\) adsorption in MOF-74-\(M\) (with \(M = \text{Mg}, \text{Ca}\), and the first row of transition metals) constitutes a sub-set of our study and serves as a benchmark. But, while that study is limited to only \(\text{CO}_2\) adsorption, we go beyond that by considerably extending the list of possible metals and also studying adsorption of \(\text{H}_2\), \(\text{CH}_4\), and \(\text{H}_2\text{O}\). The effect of water is particularly important in that it is always present in the form of humidity in flue gases and might pre-adsorb at the unsaturated metal sites of MOF, hindering the adsorption and transport properties of other target molecules.49

II. COMPUTATIONAL DETAILS

To explore the binding configurational space in terms of metal species and adsorbing molecules we use density functional theory with the van der Waals density functional \(\text{vdW-DF}\)50–53 as implemented in VASP.54–56 We have already successfully applied \(\text{vdW-DF}\) to investigate the adsorption of small molecules in MOFs and nano-structures in numerous other studies.56–79 In particular, \(\text{vdW-DF}\) is crucial for correctly describing the binding of water.56
Due to the large unit cell of MOF-74 with 54 atoms, the total energy was sampled at the Γ-point only. Projector augmented-wave theory (PAW) combined with a well-converged plane-wave cutoff of 480 eV were used to describe the wave functions. The convergence threshold for the total energy was set to 1×10−5 eV, ensuring an accurate calculation of the adsorption energies. The internal geometry and unit cell of MOF-74 were fully relaxed for all M using vdW-DF (empt) and fully loaded with H2, CO2, H2O, and CH4) until the force and stress criteria of 1×10−3 eV Å−1 and 1×10−3 eV Å−3 were satisfied. For the study of the electronic structure of these MOF materials we carried out the Bader analysis using the fast implementation proposed by Henkelman et al. Graphical manipulations were carried out using J-ICE.

Our calculations start from the experimental hexagonal structure of MOF-74-Zn with space group R3̅ and a = 25.932 Å and c = 6.836 Å and 54 atoms per unit cell. We then swap out the Zn atoms in sequence with Be, Mg, Al, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Sr, Zr, Nb, Ru, Rh, Pd, La, W, Os, Ir, and Pt, respectively. Originally, we also considered Y, Mo, Ag, Ce, and Au, however, their respective MOF structures are relatively unstable preventing their convergence. Since some of these metals present an open-shell electronic structure, we adopted a collinear spin-corrected treatment, with an appropriate approximation for the vdW-DF part. We impose an anti-ferromagnetic alignment of the spins on the six metal ions in the unit cell, according to previous experiments and theoretical observations. Six H2, CO2, H2O, and CH4 molecules per unit cell are then adsorbed at the uncoordinated metal sites M in the MOF nano-pores, reproducing scenarios of channel saturation of previous X-ray and neutron-diffraction experiments.

### III. RESULTS

#### A. Properties of the Empty MOF

We begin our discussion by commenting on the structural characteristics of the empty MOF-74. Table I shows the structural parameters and other relevant quantities of MOF-74 after complete structural relaxation at 0 K. There is not a simple explanation for the dependence of the lattice parameters on the metal species. But, it is interesting to see that Os results in the smallest unit cell, while Ca results in the largest. The significant difference between them can be associated to the ionic radii of Ca2+ ≈ 1.00 Å and Os2+ ≈ 0.49 Å ions when in a penta-coordinated oxygen environment (as found in MOF-74-M). Note that the other metal species do not necessarily follow such a simple trend, and hence we cannot extrapolate a general dependence of ionic radius vs. volume.

We also simulated the powder X-ray spectra of a few selected MOFs obtained throughout the HTS procedure, resulting in important fingerprints for their future synthesis (see Supplementary Materials).

It is also interesting to study the Bader charges of the metal ions in the MOF. Figure I analyzes the 25 situations in Table I and plots the number of occurrences of Bader charges Q_M. From this figure we see that most of the metal species in MOF-74 display charges ranging from 1.0 to 2.0 e, consolidating the picture of divalent metal ions. Exceptions are Al, which carries almost a 3+ charge as expected, and Cu, which remains as Cu(I). Our finding also suggest that Rh, Pd, Os, Ir, and Pt remain weakly charged preserving their noble metal characteristics. The local oxygen environment experienced by the metal species of MOF-74 resembles a “surface termination” of the corresponding binary oxides, thus explaining the charge nature of these ions. Note that the charge characteristics of such metal ions reflects their reactivity towards the adsorbates.

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| M  | Z  | a  | c  | V   | Q_M |
|----|----|----|----|-----|-----|
| Be | 4  | 25.655 | 6.663 | 3797.877 | 1.6 |
| Mg | 12 | 26.084 | 6.863 | 4043.947 | 1.5 |
| Al | 13 | 25.402 | 6.565 | 3668.630 | 2.6 |
| Ca | 20 | 25.454 | 7.591 | 4259.190 | 1.5 |
| Sc | 21 | 23.675 | 7.334 | 3559.960 | 1.9 |
| Ti | 22 | 23.669 | 7.210 | 3498.429 | 1.8 |
| V  | 23 | 25.254 | 7.000 | 3868.982 | 1.6 |
| Cr | 24 | 26.171 | 6.525 | 3870.148 | 1.5 |
| Mn | 25 | 26.242 | 7.082 | 4223.524 | 1.4 |
| Fe | 26 | 26.010 | 6.711 | 3931.742 | 1.3 |
| Co | 27 | 26.078 | 6.872 | 4047.173 | 1.3 |
| Ni | 28 | 25.688 | 6.188 | 3536.291 | 1.1 |
| Cu | 29 | 26.271 | 6.138 | 3668.332 | 0.8 |
| Zn | 30 | 26.142 | 6.875 | 4068.779 | 1.2 |
| Sr | 38 | 26.683 | 6.710 | 4137.427 | 1.6 |
| Zr | 40 | 23.455 | 7.530 | 3587.630 | 2.0 |
| Nb | 41 | 27.031 | 6.414 | 4058.779 | 1.4 |
| Ru | 44 | 27.061 | 6.119 | 3880.592 | 1.3 |
| Rh | 45 | 25.833 | 6.804 | 3932.355 | 1.3 |
| Pd | 46 | 25.570 | 6.432 | 3932.482 | 1.1 |
| La | 57 | 26.672 | 6.431 | 3962.091 | 2.2 |
| W  | 74 | 26.960 | 6.177 | 3888.314 | 1.6 |
| Os | 76 | 26.480 | 4.977 | 3984.552 | 1.2 |
| Ir | 77 | 26.020 | 6.796 | 3984.552 | 1.2 |
| Pt | 78 | 26.560 | 6.511 | 3977.779 | 1.2 |
B. Adsorption Characteristics

Our discussion now moves to the analysis of the adsorption energies, which determine if molecular adsorption is favorable. We define the adsorption energy as in Eq. (1)

\[
\Delta E = E_{\text{MOF}+\text{M}} - E_{\text{MOF}} - E_{\text{M}(g)},
\]

where \(E_{\text{MOF}+\text{M}}\), \(E_{\text{MOF}}\), and \(E_{\text{M}(g)}\) are the total energy of MOF with molecules adsorbed in its nano-pore, the energy of the empty MOF, and the energy of the molecule in its gas phase geometry, respectively. Note that throughout the manuscript we will also refer to the adsorption energies as binding energies. Two interesting deformation contributions \(\delta E_M\) and \(\delta E_{\text{MOF}}\), which are clearly connected to the adsorption process, are defined in Eqs. (2) and (3):

\[
\delta E_M = E_{\text{M,in} \cdot \text{MOF}+\text{M}} - E_{\text{M}(g)},
\]

\[
\delta E_{\text{MOF}} = E_{\text{MOF,in} \cdot \text{MOF}+\text{M}} - E_{\text{MOF}},
\]

where \(E_{\text{M,in} \cdot \text{MOF}+\text{M}}\) and \(E_{\text{MOF,in} \cdot \text{MOF}+\text{M}}\) are the energies of the molecule and the MOF in their adsorption geometries. \(\delta E_M\) and \(\delta E_{\text{MOF}}\) express the cost in energy that both adsorbate and MOF have to pay during the adsorption process. The \(\delta E_M\) term also contains the lateral interactions between adjacent molecules, which in turn depend on the electronic characteristic of each molecule and their mutual positions. Note that both \(\delta E_M\) and \(\delta E_{\text{MOF}}\) contributions are related to the re-arrangement of the molecular and MOF geometries in order to maximize the binding interaction. \(\delta E_M\) and \(\delta E_{\text{MOF}}\) are obtained by partitioning the adsorption energy, and thus they are naturally enclosed in the definition of \(\Delta E\) in Eq. (1). Finally, it is possible to define an adsorption quantity \(\Delta E^C\) free of any deformation contributions as

\[
\Delta E^C = \Delta E - \delta E_M - \delta E_{\text{MOF}}.
\]

Table II is the main result of this paper and collects the calculated values for the quantities defined in Eqs. (1) – (4).

We begin by making some observations on the evolution of the structures of these MOF-74-\(\text{M}\) once the adsorbing molecules is introduced. A first glance tells us that the pore size and volume of the MOFs decrease when molecules are adsorbed in their structures (see Table S1 in the Supplementary Materials). The extent of volume change is balanced between the size of the adsorbing molecules and the nature of the adsorption interactions in Table II. For example, we observe the “clog up” of the MOF nano-pore when six \(\text{CH}_4\) molecules are concomitantly adsorbed, hence increasing the lateral molecule to molecule interaction as demonstrated by the \(\delta E_M\) in Table II. The presence of large, attractive \(\delta E_M\) values contributes to “unphysically” lowering the overall \(\Delta E\). Figure 2 shows the perturbation introduced in the volume of MOF-74-\(\text{M}\) after six \(\text{CH}_4\) molecules are introduced in its cavity. The trend in volume changes is not directly correlated to \(\Delta E\), but rather to \(\delta E_M\) (see Table II), which combines the molecular deformations and the lateral interactions experienced by the molecules during the adsorption. In the case of \(\text{CH}_4\) the intermolecular interactions are considerably stronger and keep the MOF structure from swelling apart, which could occur otherwise given the substantial volume of six \(\text{CH}_4\) molecules in such a small pore (diameter \(\sim13\) Å). Similar conclusions can also be drawn for \(\text{H}_2\), \(\text{CO}_2\), and \(\text{H}_2\text{O}\), however, the effect on the respective volume changes is smaller. The different changes in volume due to the diverse nature of the MOF/molecule interaction and the molecular volume again reflect the high structural flexibility displayed by these porous materials. In other words, the MOF structure responds differently to different molecules, manifesting significant and unprecedented molecular recognition effects that could be exploited for sensor applications and are investigated in a forthcoming publication.

The diverse molecular recognition displayed by these MOFs is also revealed by the binding energies \(\Delta E\) of \(\text{H}_2\), \(\text{CO}_2\), \(\text{CH}_4\), and \(\text{H}_2\text{O}\) in MOF-74-\(\text{M}\) (see Table II).
In general, we find that the $\Delta E$s of these molecules are substantially different in magnitude by tens of kJ mol$^{-1}$ and follow a precise trend $\text{H}_2O \gg \text{CO}_2 \gg \text{CH}_4 \gg \text{H}_2$. The consistent gap between the adsorption energies of different molecules indicates that such MOFs can be efficiently used in filters for the separation of blended gases.

According to the electrostatic complementarity principle (donor-acceptor), the metal species of the MOF structures act as Lewis acid laking in electrons, whereas the adsorbing counterparts (in general oxygen atoms) behave as Lewis base providing electrons. It is well established that in the case of $\text{H}_2O$ the driving force dictating the molecular adsorption at the metal site is its strong dipole moment, whereas the adsorption of $\text{H}_2$, $\text{CO}_2$, and $\text{CH}_4$ relies on weak van der Waals forces. This is demonstrated by the $\Delta E$ of Table [II]. Water clearly remains the preferred molecule for the metal sites, with the exception of some noble metals i.e. Rh, Pd, Os, Ir, and Pt (see below), implying that performance for gas-storage applications can be hindered in moisturized environments. The presence of water in these nano-porous materials is scarcely documented in the literature[26,33] but remains a major operational problem; it is partly for this reason that non hydro-soluble MOFs such as fluorinated MOFs are being developed.[37,43]

It is also interesting to look at the different adsorption energy contributions, i.e. $\delta E_M$, $\delta E_{\text{MOF}}$, and $\Delta E^C$ in Table [II]. As anticipated, the negative sign of the $\delta E_M$ is simply due to the attractive intermolecular interactions and their magnitudes only depend on the molecular size and the extent of pore reconstruction, the latter being connected to the nature of the metal ions. On the other hand, the sign of the $\delta E_{\text{MOF}}$ is always positive (with very few exceptions) and is thus an indication that the MOF undergoes an unfavorable reconstruction when the molecule is adsorbed. In the majority of the cases the $\delta E_M$ is larger in magnitude than $\delta E_{\text{MOF}}$.

In general, the calculated $\Delta E$s of Table [II] are in good agreement with previous experimental and computational data.[22,28,38,41] Our data reproduces the $\Delta E$ order established for $\text{CO}_2$ in MOF-74-Mg > MOF-74-Ni > MOF-74-Co, consistent with previous experimental investigations.[23] The adsorption energies calculated for most of the molecules are slightly overestimated by 2 – 5 kJ mol$^{-1}$ from the experimental data (where available), which is typical for the vdW-DF functional.[28] Nevertheless, inclusion of the zero-point energy and temperature effects via phonon calculations (not performed in this study) can lower the $\Delta E$s and bring them in better agreement with experimental data.[22,28,41] $\Delta E^C$, rather than $\Delta E$, is more appropriate for comparison with experimental data, as it is not affected by the spurious lateral interactions introduced by the high-loading regimes imposed in our simulations (six molecules per cell).

| $\text{H}_2$ | $\text{CO}_2$ | $\text{CH}_4$ | $\text{H}_2O$ |
|----------------|----------------|----------------|----------------|
| $\Delta E$ | $\Delta E^C$ | $\delta E_{\text{MOF}}$ | $\delta E_M$ |
| Be | -16.5 | -15.1 | 0.4 | -0.8 |
| Mg | -15.8 | -15.5 | 0.3 | -0.7 |
| Al | -19.8 | -18.6 | -0.9 | -0.3 |
| Ca | -18.7 | -19.5 | 1.2 | -0.4 |
| Sc | -19.6 | -19.6 | 0.6 | -0.6 |
| Ti | 1.4 | -18.6 | 12.0 | 8.0 |
| V | 20.0 | -19.0 | -0.6 | -0.4 |
| Cr | -19.8 | -19.6 | 0.2 | -0.5 |
| Mn | -19.0 | -19.1 | 0.5 | -0.3 |
| Fe | -19.8 | -19.1 | -0.2 | -0.4 |
| Co | -19.8 | -19.5 | 0.5 | -0.4 |
| Ni | -19.1 | -18.0 | 0.3 | -1.5 |
| Cu | -a | -a | -a | -a |
| Zn | -20.5 | -19.4 | 0.4 | -2.0 |
| Sr | -18.6 | -19.4 | 1.2 | -0.4 |
| Zr | -17.8 | -17.1 | 0.2 | -0.9 |
| Nb | -20.7 | -20.7 | 0.2 | -0.2 |
| Ru | -20.5 | -19.5 | 0.3 | -0.7 |
| Rh | -20.8 | -19.9 | -0.5 | -0.4 |
| Pd | -19.5 | -19.0 | 0.1 | -0.7 |
| La | -20.2 | -18.7 | -0.9 | -0.7 |
| W | -21.9 | -20.6 | -0.9 | -0.4 |
| Os | -19.1 | -9.4 | 0.3 | -10.0 |
| Ir | 20.4 | -19.5 | -0.4 | -0.4 |
| Pt | -19.3 | -18.4 | -0.4 | -0.6 |

$^a$Simulation considered not converged since we observe unphysical molecular dissociations due to huge structural strains.
Somewhat surprisingly, the data in Table I demonstrates that for most cases the adsorption energies of H₂ in MOF-74 only marginally change with the metal species. It follows that the currently synthesized MOF-74-Mn, MOF-74-Fe, MOF-74-Co, MOF-74-Ni, and MOF-74-Zn are already “as good as it gets” for the purpose of hydrogen storage. A loading of six molecules in MOF-74-M per unit cell corresponds to a hydrogen-storage capacity of 1.6 mass% and 4.9 g H₂ L⁻¹. Although not investigate here, secondary binding sites exist in MOF-74 and the unit cell can hold 12 H₂ molecules under high pressure, corresponding to theoretical values of 3.2 mass% and 9.9 g H₂ L⁻¹ volumetric uptake. These numbers are in the mid-range of physisorption-based nano-porous hydrogen-storage materials. Again, co-presence of H₂O in the MOF environment is a problem for hydrogen-storage applications, as it degrades the storage capacity even more due to the large binding energies of water compared to H₂. Note that the sign of ∆E for H₂ in MOF-74-Ti suggests that this adsorption is thermodynamically prohibited.

Several computational studies have investigated the interaction of CH₄ with MOF-74, often using plain LDA functionals which incorrectly describe the dominating van der Waals interactions relevant for the adsorption. Note that here we employ an exchange-correlation functional that is not parametrized and hence capable of capturing the diverse nature of the molecular interactions with all metals. On the other hand, the empirical method DFT+U works well only for a few metals where the empirical parameters (the C₆ coefficients) are extracted from ab initio data; this is not appropriate for metals whose C₆ coefficients are extrapolated from lighter elements along the group. This would explain why Park et al. obtained very similar ∆E for the metal ions of the first transition metal row. Furthermore, the C₆ obtained by Grimme et al. were derived for atomic species and not ions, hence not reflecting the nature of the metal ions in MOF-74 as demonstrated by the Bader charges in Table I and Fig. I.

**D. Competition of H₂O and CO₂ Adsorption**

Our analysis now moves to the comparison of the computed binding energies for CO₂ and H₂O. The top panel of Fig. 3 shows that in most cases the ∆Es for CO₂ in MOF-74-M oscillate between 40 and 60 kJ mol⁻¹. However, when adsorbing CO₂ in MOF-74-Al, MOF-74-La, and MOF-74-Nb, we observe a complete chemisorption of CO₂ at the metal site, sharing electrons with the MOF structure and therefore causing a steep increase of the adsorption energies. From a practical point of view, note that strong chemi-adsorption prevents the re-use of MOFs as the molecule is now fully integrated in the MOF structure and its chemical identity is unrecoverable. In the Supplementary Materials we show the irreversible structural and molecular changes occurring in MOF-74-Al and MOF-74-La loaded with CO₂.

Very interesting are also MOF-74-Be, -Ca, and -Cr, in which we observe a complete desorption of CO₂ molecules from the metal sites despite the considerable adsorption energies reported in Fig. 3. MOF-74-Be is thus a special case and we do not list it together with the other noble metals that have strong affinity towards CO₂. To quantify this effect, we report the molecule/metal distances in Table S1 of the Supplementary Materials. The small affinity of CO₂ for the metal species (i.e. Be, Ca, and Cr) causes the molecules to reorganize close to each other, establishing strong attractive intermolecular interactions, decreasing the overall ∆Eₘ (see the Supplementary Materials). As mentioned before, large values of ∆Eₘ spuriously affect the final magnitude of ∆E, whereas the ∆Eₐq are more appropriate as reference for further comparisons. Similar (but smaller) is the behavior of CO₂ with some metal ions such as Ti, Zr, and W.

The bottom panel of Fig. 3 shows the binding energy of CO₂ relative to that of H₂O. In the majority of the metals investigated, water binds stronger than CO₂, reaching occasionally more than 100 kJ mol⁻¹, see for example MOF-74-Al, -Sc, -V, -Fe, -Sr, -Nb, -La, and -W. A recent attempt of increasing the CO₂ affinity (compared to water) was proposed by Planas et al. functionalizing the metals species of MOF-74-Zn with amines with the effect of increasing the adsorption energy of CO₂. However, the reactivity of water was not tested. A closer look at the adsorption geometries for these models explains the reasons of such high ∆E values—we observe the incipient formation of strong hydrogen bonds with...
oxygen atoms that coordinate the metal ions, thus explaining the large structural deformation subsequent to adsorption (see $\delta E_{\text{MOF}}$ in Table I). For these latter cases we have plotted the density of states (DOS) of both MOF and water molecules before and after the adsorption, demonstrating the nature of the chemi-adsorption (see the Supplementary Materials). Although from the DOS we notice the injection of some molecular states in the band structure of the MOF, the geometry of the adsorption conformation does not assist the water dissociation, in contrast to what is largely observed for surfaces of the respective metal-oxides.

As mentioned, the noble metals Rh, Pd, Os, Ir, and Pt are special in that they invert the trend of the adsorption energies for CO$_2$ and H$_2$O. The initial adsorption conformation for these cases consists of water molecules in contact with the metal species (i.e. Rh, Pd, Os, Ir, and Pt). This situation is immediately disrupted due to the redox nature of those metals. For these cases, the noble metals act as donor competing with the oxidizing oxygen of water leading to unfavorable interactions, i.e., repulsions. After complete structural relaxation, the oxygen atoms of H$_2$O molecules are found far from the noble metal. Water molecules are entirely displaced from the original binding pocket, assuming a new binding conformation that favors the formation of hydrogen bonding with atoms of the linkers (see Fig. 1). We did not observe strong interactions between the protons of H$_2$O molecules and the metal sites, a situation that is extremely favorable in simpler systems such as water on platinum surfaces and other noble metals.$^{23,24}$ To this end, the analysis of the Bader charges of the metal ions explains intuitively the nature of the molecule-metal interaction. Once the water molecules enter in contact with MOF-74-$M$ (with $M = \text{Rh, Pd, Os, Ir, and Pt}$) we find that the charge of the metal ion is unaltered since water molecules do not directly perturb the ion. Although for Rh, Pd, Os, Ir, and Pt the $\Delta E$s of CO$_2$ adsorption are always larger than the ones for H$_2$O, we find that the CO$_2$ molecules also remain slightly separated from the metal ions (see the corresponding distances in the Supplementary Materials) compared to other transition metals, demonstrating that such noble metals prefer a reducing environment.

IV. CONCLUSIONS

In this study we sample the adsorption configurational space of small molecules in MOF-74. In particular, we utilize high-throughput screening to investigate the adsorption properties of H$_2$, CH$_4$, CO$_2$, and H$_2$O in MOF-74-$M$ with $M = \text{Be, Mg, Al, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Zr, Nb, Ru, Rh, Pd, La, W, Os, Ir, and Pt}$. We demonstrate that HTS can reveal important information about these systems, which can aid in accelerating the engineering and improving of existing metal organic frameworks for hydrogen storage, carbon capture, and gas-separation.

Independently of the metal species of MOF-74-$M$, we find a consistent gap between the adsorption energies of different molecules, i.e. from strongest to weakest H$_2$O $\gg$ CO$_2$ $> CH_4$ $> H_2$, thus concluding that these materials can be efficiently used in filters for the separation of blended gases. Furthermore, H$_2$O is always present in the form of humidity in the operational environment of MOFs, and we find that it can significantly decrease the adsorption and transport properties of target molecules. We further find that metal species at the left of the periodic table are less effective in capturing CO$_2$, displaying a larger affinity for H$_2$O—an indication that these MOFs are susceptible to moisturized environments. Our analysis suggests an improving affinity for CO$_2$ when moving towards the right along the transition metal series. On the other hand, our data does not suggest a systematic trend along each group. The redox characteristics of noble metals such as Rh, Pd, Os, Ir, and Pt in MOF-74 increase the interaction with CO$_2$, while the affinity for water is almost suppressed. This is an important indicator and such metals are thus interesting candidates for the preparation of alternative MOFs that are less susceptible to humidity, with direct employment in carbon-capture applications.

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