

Modelling of hydrogen adsorption in the metal organic framework MOF5

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Abstract

Metal organic frameworks are formed by rigid organic spacer molecules linked by metal ions into a three-dimensional nano porous structure. The large internal surface (up to $4500 \text{ m}^2 \text{ g}^{-1}$) provides abundant sites for the adsorption of small molecules like hydrogen, which currently generates significant interest for their potential application as reversible hydrogen storage matrix. A prerequisite for hydrogen storage at ambient conditions is that the interaction strength is sufficiently large. Using VASP ab initio computer calculations the adsorption interaction strength for MOF5 is found to be of the order of 70 meV per H_2 molecule, where the main adsorption interaction is with the oxygen atoms. Such value compares well with adsorption experiments on MOF5 and it exceeds that obtained in nanostructured pure carbon materials. The $J = 0$ to $J = 1$ rotational transition of the H_2 determined from inelastic neutron scattering results of Rosi et al. [N.L. Rosi, J. Eckert, M. Eddaoudi, D.T. Vodak, J. Kim, M. O'Keeffe, O.M. Yaghi, Science 300 (2003) 1127] is compared to the simulation results, and a hydrogen self diffusion coefficient is estimated.

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1. Introduction

Efficient and facile hydrogen storage is required for the realisation of a hydrogen based energy economy. Recently significant interest has been raised in the field of light, nanoporous metal organic framework (MOF) materials in view of hydrogen adsorption on their internal surfaces [1–5]. Yaghi and co-workers showed that these crystalline materials can adsorb up to 2 wt% H_2 at temperatures of 77 K and pressures of a few bars. The frameworks consist of rigid organic spacer molecules that are bonded into a three dimensional structure by the formation of metal complexes that fix the direction of the spacers (Fig. 1). The spacer molecules

contain aromatic rings that make them rigid building units.

For hydrogen storage using an internal surface adsorption process three factors are of major importance. First there needs to be sufficient interaction strength to make adsorption possible at reasonable temperatures and pressures. Second, there needs to be a large amount of surface per gram material, and third the internal surface should be easily accessible to the hydrogen molecules, i.e., the pore size along the diffusion path should not be smaller than the kinetic diameter of H_2 which equals $\sim 2.9 \text{ \AA}$. The first factor limits the applicability of pure carbon materials at ambient temperatures as was shown in previous experimental work on carbon nanotubes, and activated carbons. Although their BET surface area's of ~ 2000 and $600 \text{ m}^2 \text{ g}^{-1}$, respectively [6] are sizeable, the adsorption interaction

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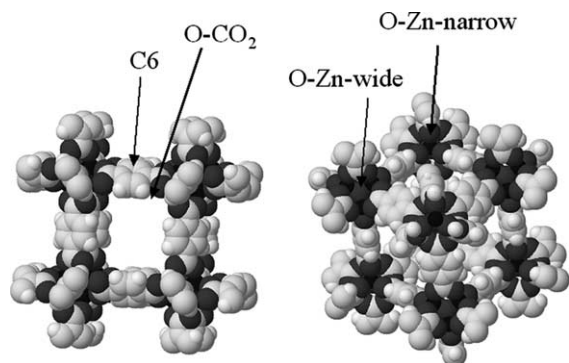


Fig. 1. The minimised unit cell of MOF5 viewed from two different directions. Left the open pore structure is visible. White spheres: hydrogen, light gray: carbon, dark grey: oxygen, black: zinc. The hydrogen adsorption sites are indicated by arrows (see also Fig. 2).

strengths on the carbon materials is about 600 K, i.e., 55 meV per adsorbed H_2 molecule. As was shown in [6], this adsorption strength is sufficient for adsorption below 70 K; above such temperatures the pressures become exceedingly high, and there is a reducing benefit from having the sorption material in the tank. Also theoretical calculations on H_2 adsorbed on various aromatic carbon compounds showed limited interaction strengths [7].

The MOFs have very large internal surfaces so if by chemical modification the adsorption interaction strength could be increased this would provide a pathway towards successful hydrogen storage. As a first step it should be determined at which sites hydrogen can adsorb, and what the interaction strengths are. For this reason we performed density functional theoretical calculations of MOF5, one of the first metal organic framework materials that shows promising hydrogen adsorption [1]. Currently no direct experimental data are available on the position of preferential hydrogen sites, but there exists neutron spectroscopic evidence for at least two different adsorption sites with considerable interaction strength [1].

In this contribution we describe the results of ab initio computer calculations on the full MOF5 structure with hydrogen molecules adsorbed in it. The adsorption energies and sites as well as values of the hydrogen diffusion coefficient will be presented. The results are compared to neutron spectroscopy and other experimental data in [1].

2. Details of the calculations

The calculations were performed using density functional theory (DFT) in the generalised gradient approximation (GGA) as implemented in the VASP plane wave pseudo-potential code [8]. Generally DFT codes have limitations in reproducing long-range dispersive interac-

tions like the van der Waals interactions (see, e.g., [9] for a discussion). Recently, however, it was shown that DFT with GGA pseudo potentials give good agreement of the adsorption energy with experimental results for hydrogen adsorbed on carbon [10] and for alkanes adsorbed in zeolites [11]. We will therefore compare the computational results with the experimental results that are available. Furthermore, the results are compared to those obtained using the Møller–Plesset (MP2) perturbation theory as reported in [12]. The latter results could only be obtained on selected molecules that mimic fragments of the MOF5 structure because of the large computational costs of MP2 compared to VASP.

The model of the primitive cell of the MOF5 matrix contains 106 atoms. The initial structure from the X-ray diffraction at room temperature was first relaxed by a 2 ps MD at a temperature of 5 K with a step size of 1 fs. Subsequently the structure was minimised, and the energy of the minimised configuration was calculated. In order to obtain the potential H_2 adsorption sites, up to 23 H_2 molecules were included in the simulated model simultaneously, making the total of atoms in the primitive cell 152. A 4 ps MD simulation was performed starting at temperatures of 100 K, and linearly cooling to 1 K. In this way the molecules were free to diffuse to different sites, and with reducing temperature were first trapped in the strongest binding sites. After this MD the structures were minimised further, which resulted then only in optimised orientations of the H_2 molecules on their sites.

The adsorption energy for different sites was calculated from the difference in energy of the minimised structure with adsorbed H_2 , with the same structure where a specific H_2 has been removed, and corrected for the energy of a free H_2 molecule in the same (but otherwise empty) cell. The average adsorption energy for 23 H_2 molecules was also calculated from the difference of filled structure and empty structure.

After preferential sites had been identified the potential barrier for the $J = 0$ to $J = 1$ rotational transition of the hydrogen molecule was calculated classically by stepwise rotation of the molecule over 15° steps and calculation of the energy while fixing all other atoms.

Molecular dynamics simulations were performed at temperatures of 5, 38 and 78 K using a 1 fs timestep and simulation times up to 4 ps. These calculations were restricted to 4 ps because of the exceedingly long computing time (weeks).

3. Result and discussion

3.1. Adsorption energies and sites

The minimised conformation of empty MOF5 has a cubic structure similar to that of the reported room

Table 1
Minimised structure of MOF5 reduced to spacegroup 202 symmetry

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>
Zn	32f	0.2936	0.2936	0.2936
O	96i	0.2763	0.7147	0.3663
O	8c	0.25	0.25	0.25
C	48g	0.1114	0.25	0.25
C	48g	0.0537	0.25	0.25
C	96i	0.2777	0.7115	0.4730
H	96i	0.9509	0.7012	0.8179

Lattice parameter: 25.8399 Å. F m 3 (nr 202) is a subgroup of the F m 3 m (nr 225) reported in [1,13], and allows for a slight rotation of the benzene rings away from the higher symmetry positions.

temperature structure [13]. When looking for symmetry the cubic spacegroup 202, F m-3 is found with a lattice parameter $a = 25.669$ Å. The corresponding atomic positions found after restricting them to the symmetry of the spacegroup are given in Table 1. The difference with the structure in [13] is mainly visible in the slight deviation of the orientation of the benzene rings from their experimentally reported higher symmetry positions. The lattice parameter (at zero temperature) compares well with that of reported RT one: $a = 25.885$ Å. The fact that the minimised space group at zero temperature is not exactly the same as, but closely related to, the experimental one at room temperature is not surprising in view of the presence of thermal motions at RT.

Four sites with the largest adsorption energies that were found are listed in Table 2. Such value compares favourably with the 55 meV per H₂, which was found experimentally for nanostructured carbon materials such as single walled carbon nanotubes, activated carbons and graphitic fibres [6]. An increase of the adsorption energy promotes the adsorption at somewhat higher temperatures than for the nanocarbons, and indicates that this metal organic framework is promising in this respect. The future task is to tailor the structure such that the adsorption energy as well as the number of adsorption sites is optimised, while still maintaining a low weight of the matrix.

Table 2
The four different preferential H₂ adsorption sites identified by the computer simulations for MOF5

Site	$\delta E_{\text{adsorption}}$ (meV)	Sites/cell	Max. wt%	Rotation barriers (meV)	Bond distance (Å)	Fluoro $\delta E_{\text{adsorption}}$ (meV)	Bromo $\delta E_{\text{adsorption}}$ (meV)
C6	-66	48	1.5	0 – 3	3.44	-74	-74
O-Zn-wide	-70	32	1.0	10 – 13	2.82	-73	-73
O-Zn-narrow	-70	32	1.0	0 – 1	3.18	-86	-101
O-CO ₂	-72	96	3.0	2 – 5	2.90	-77	-74

$\delta E_{\text{adsorption}}$ indicates the adsorption energy per H₂, sites/cell indicates the number of available similar sites in the unit cell, the wt% indicates the maximum weight percentage reached when all these sites would be occupied (however, such full occupation can only occur at very low *T*, and when there is no hindrance between different occupied sites). The approximate rotation barriers are calculated classically from stepwise rotation of the H₂ molecule over two different axes. The bond distance is the calculated distance between the adsorbed H₂ molecule and the benzene ring for the C6 site and the distance to the nearest O atom for the other three sites. The last two columns give the adsorption energy of, respectively, fluorine and bromine modified MOF5.

In [1] maximum total hydrogen adsorptions are given of 4.5 wt% at 78 K and 1 bar. However, in [2] weight percentages of 1–2% are indicated under similar conditions for MOF5 and a few related MOF structures. Recently Panella and Hirscher [14] determined similar values at 77 K for MOF5 (see also below). The reason for the higher maximum weight percentages in Table 2 may be that in the table each site is assumed to be occupied, where it can actually be the case that there is steric hindrance from the different hydrogen molecules preventing that all the sites can be occupied simultaneously. When searching for such potential hindrance especially the O-CO₂ appears to hinder the same neighbouring sites as well as hinder the O-Zn-narrow and wide sites. Another factor is that the diffusion through pores may become more difficult as soon as there is hydrogen loaded in the system, and this may effectively make the full occupation of all possible sites kinetically more difficult. These factors may effectively restrain the system from reaching full occupation of the identified sites in a diluted system; a reduction of a factor of 2 alone is possible if one assumes effective mutual exclusion of the O-CO₂ site and others. A factor ~4 reduction of the available sites is required for agreement with [14].

The experiments in [14] indicate a weight percentage of up to 1.6 at 77 K and >10 bar, and 0.16 wt% at 293 K and 60 bar. In these 77 K adsorption data there will also be contributions from sites with lower adsorption energies than in Table 2 because applying larger pressures showed that the system was saturated. At a pressure of 3 bar we may assume that the sites with the strongest adsorption interaction are occupied preferentially; Ref. [14] then indicates H₂ absorption of 1.45 wt%. In order to determine if these data could be consistent with the calculated adsorption energies we use the formula given in [6]. This equation relates the adsorption energy $E_{\text{adsorption}}$, the site coverage θ , the temperature *T* and pressure *P*:

$$P = C' \sqrt{T} \exp\left(-\frac{E_{\text{adsorption}}}{k_B T}\right) \frac{\theta}{1 - \theta}, \quad (1)$$

where C' is a constant. Assuming that 1.45 wt% out of the total of 1.6 wt% is covered at 78 K and 3 bar this leads to $\theta \approx 0.91$. At 298 K and 60 bar the coverage is reported to be $\approx 0.16 \text{ wt\%/1.6 wt\%} = 0.1$. Then one can deduce that the adsorption energy should be of the order of $\sim 730 \text{ K}$, which is consistent with the value of $\sim 770 \text{ K}$ (70 meV) found in the calculations.

The sites identified have in common that the hydrogen is closest to a certain oxygen on the benzoic-acid (Fig. 2). The C6 site is different because here it adsorbs directly on the flat surfaces of the benzene ring. The difference between the O–Zn-wide and narrow sites is a difference in orientation of H_2 with respect to the benzene rings. For the O–Zn-wide site the H_2 can approach the O a little closer as can be observed from the distance listed in Table 2. The charge density maps show that there is a path with higher charge density from the hydrogen atoms towards the nearest oxygen. In Fig. 3 an example is shown of such a graph. This indicates that for the adsorption the main interaction is with these oxygens. Such finding suggests that one may modify the MOF by making the oxygen more accessible, or have more of them in the system.

Apart from comparing with experimental results for the adsorption energy, one may compare these VASP results with those obtained with MP2 perturbation theory on specific molecular fragments as reported in [12]. Sagara et al. report adsorption energies of 5.27 for the adsorption to a H_2 -1,4-benzenedicarboxylate- H_2 molecule, and 6.86 kJ/mol at the corners of a zinc oxide corner of a $\text{Zn}_4\text{O}(\text{HCO}_2)_6$ molecule. These values amount

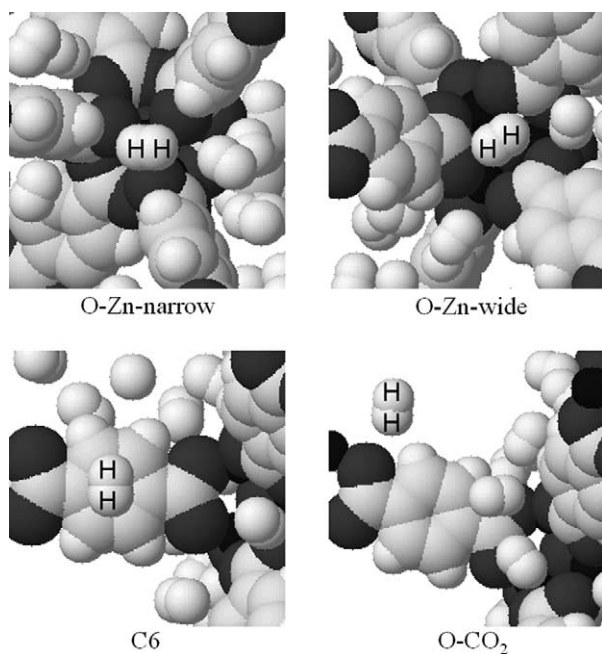


Fig. 2. The main different sites of H_2 identified by the computer simulations. The hydrogen molecule is indicated with HH.

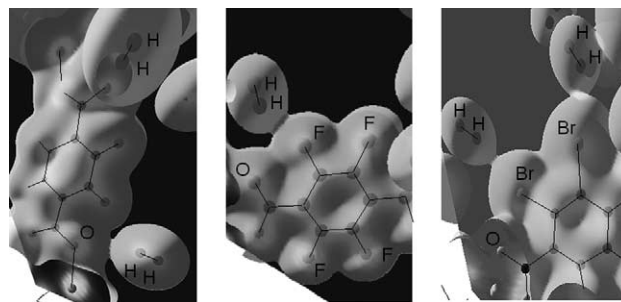


Fig. 3. A view in the charge density distributions of the simulations. *Left.* MOF5: the adsorbed H_2 in the O– CO_2 site (bottom HH) has an increased charge density along the path to the nearest oxygen. The top H_2 is also having such ‘bond’ to the nearest O. *Middle.* The same site for the fluoro-MOF5 shows increased charge density along the path H_2 –F, while it does not reach the O. *Right.* For the bromo-MOF5 the bond appears also to the Br.

to 55 and 71 meV per H_2 , respectively. Clearly it is an approximation to compare these molecules with MOF5, but nevertheless the values are of similar magnitude as what is reported in this manuscript using VASP with GGA pseudo potentials.

3.2. Rotational tunnelling and mobility of the hydrogen molecule

The rotation of the hydrogen molecules around an axis results in calculated rotational energy barriers listed in Table 2, with some variation on the axis that is chosen for the rotation. The rotational barrier could be higher for the O–Zn-wide site because here the hydrogen manages to get closer to the oxygen. The inelastic neutron scattering (INS) data reported in [1] show that the rotational tunnelling spectra for $J=0$ to $J=1$ transition have at least two peaks that are shifted down to 10.3 and 12.1 meV, respectively, from the value of the free hydrogen molecule (14.7 meV). For the lower two hydrogen loadings shown in [1] the second peak has an intensity that is 2–4 times larger. In order to relate a barrier height $|V|$ to the rotational tunnelling constant for a three-dimensional rotor the following formula can be applied [15,16]:

$$\hbar\omega = \beta \exp\left(-\alpha \sqrt{\frac{|V|}{B}}\right), \quad (2)$$

where β is close to 2 times the rotational constant B and α is close to 1. For the hydrogen molecule B equals 7.3 meV. Using Eq. (2) with the barriers in Table 2 results in rotational tunnelling constants $\hbar\omega$ of ~ 4 and ~ 8 meV for the three sites with lower barriers, respectively, which appears to be a factor ~ 2 different from the experimental values of 10.3 and 12.1 meV, but not more. The value of the rotational constant itself depends on the exact potential landscape of the site at which the hydrogen molecule is adsorbed. The shape of such

potential landscape can generally cause a mixing of the $J=0, \pm 1$ substates. Also the coupling between rotational and translational degrees of freedom can effectively alter the molecular rotational constant that is observed [12,7]. Indications that the molecule behaves in a more complex manner than a simple rotor can be found from plotting the trajectory during a molecular dynamics simulation of specific hydrogen atoms in a nuclear density graph (Fig. 4). Also phonons from the lattice will perturb the motion of the molecules, and may facilitate the rotation (phonon assisted tunnelling). The motion of the framework molecules at a temperature as low as 15 K appears to be significant, even for the limited cell size that was used: for instance an oxygen atom appears to move during the 4 ps simulation with an amplitude of ~ 0.3 Å. A more detailed calculation of the hydrogen rotational constant should take into account such factors of the environment and lie therefore beyond the scope of the present paper.

When the calculated barriers and the corresponding site abundance in Table 2 is related to these experimental data one may suggest that the O–Zn-wide site is related to the smaller peak with the larger shift, while the three other sites all give a similarly shifted peak with an added intensity that is therefore larger. We may thus conclude that the calculations indicate two different contributions to the spectrum with significant rotational barriers and intensity ratio of 1 to ~ 5.5 . This is

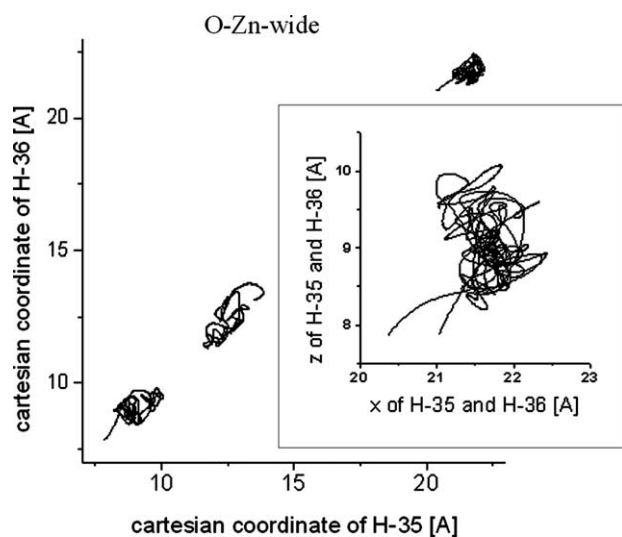


Fig. 4. The x , y , and z coordinates of one proton plotted against that of the other proton from the same hydrogen molecule adsorbed in a O–Zn-wide site. The trajectories are from a 3.6 ps molecular dynamics simulation at 15 K. The inset shows the (x, z) for the same two protons. It can be concluded from these graphs that the molecule does not behave as a simple rotor, but rather has translational and rotational degrees of freedom. At 15 K almost all molecules remain captured in their site, but for longer timescales or higher temperatures the chance is large that the molecule leaves the site spontaneously or is knocked out of it by another H_2 .

consistent with the observation in [1] of two shifted peaks with intensity ratios of up to 1 to ~ 4 .

Using molecular dynamics simulations at 15, 38 and 78 K an impression can be obtained of the value of self-diffusion coefficients. The average coefficients were calculated from the trajectories of the 23 molecules for simulation durations of ~ 4 ps each. It appears that at 78 K the simulations result in a self diffusion coefficient of $2 \times 10^{-3} \pm 1 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$, and at 38 K it is reduced down to $4 \times 10^{-4} \pm 3 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$. For 15 K the simulation duration appears to be too short to determine the diffusion coefficient in this way because then only a few of the H_2 molecules left the site in which they were adsorbed. For the higher temperatures many of the H_2 molecules travel through the whole simulated model. The error bars are large on the computed diffusion coefficients because of the differences between the individual molecules and the limited simulation time. In principle such coefficient could be determined more accurately with increasing simulation time, but this requires significantly enhanced computing resources. This indicates that the internal pore size of the system is sufficiently large to allow hydrogen transport, and also that the molecules easily diffuse between the different sites they can be temporarily trapped in. The order of magnitude of the diffusion coefficient appears to compare well with what is found experimentally for hydrogen adsorbed on nanostructured carbons like nanotubes and grafoil: at 38 K a diffusion coefficients of $2 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ is reported using quasi elastic neutron scattering results [17]. For MOF5 the diffusion coefficient appears to be equal or somewhat larger. Clearly this will also depend on the loading of the sample with hydrogen. Apparently the larger adsorption energy for MOF5 than for the nanocarbons does not limit the diffusion. The reason for this may be found in the fact that the differences in adsorption energy between the different sites are not large, and apparently also the barriers between them; then the hydrogen molecules can more or less slide along the internal surface of the MOF. Also the low temperature mobility of the MOF itself may facilitate the H_2 diffusion.

3.3. The influence of chemical modification

In order to investigate the effect of chemical modification of the MOF5 framework we calculated the minimum energy configurations and adsorption energy of MOF5 where F and Br substituted H on the C6 ring. It appears that the adsorption energy is lower for both modified compounds. For the Br compound there is significant steric hindrance between the C_6Br_4 ring and the CO_2 groups, resulting in a rotation with respect to each other. When observing the charge density maps in Fig. 3 it appears that the adsorption of H_2 on the oxygen atoms is more or less replaced by that to the larger F

or Br atoms. This may be due to a somewhat stronger interaction with the halogen atoms with their strongly polar nature. It will also play a role that the hydrogen cannot reach the oxygen any more due to steric hindrance of the large F and Br. For the O–Zn-narrow site the calculated adsorption energy becomes more negative in the sequence H, F to Br. The reason for this appears to be that for the larger halogens the hydrogen molecule can interact with more than one of them, resulting in stronger interactions. Clearly the effect of the halogen substitution is on average not large, and the added weight of the matrix reduces its usefulness too. In conclusion the modification by these halogens does show a limited modification of the adsorption characteristics.

The finding that these computer calculations indicate predominantly adsorption to the polar groups like oxygen or halogen atoms suggests that chemical alteration of the MOF should introduce additional O containing groups that could function as adsorption sites. In addition the adsorption site at the aromatic rings appears to benefit from modification of the charge density in the aromatic pi system by strongly electron withdrawing halogens. Computer simulations like the ones presented here may be used as a tool to screen the potential adsorption capabilities of chemically modified compounds.

4. Conclusions

The calculation of adsorption energies and preferential adsorption sites leads to the finding that H₂ could be stored at low temperature in four different sites with adsorption energies of around 70 meV. Such adsorption energy is almost 30% larger as that found in nano carbon systems and makes MOFs therefore relatively more promising for hydrogen adsorption. The calculations appear to compare well to neutron spectroscopic data

on the rotational $J = 0$ to $J = 1$ transition of the H₂ molecule, as far as the intensity ratio's of the expected signals are concerned and also with respect to the relative heights of the barrier for rotation. The comparison with experimental estimation of the adsorption energy coincides with the calculation to within 7%. This investigation may provide a benchmark for future work on adsorption energies that can be obtained by chemical modification of the MOFs.

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