Structural and bonding properties of small hydrocarbons inside Ca(squarate)-metal organic framework: *ab-initio* study

Sufian Alnemrat1,2,∗, Joseph P Hooper1, Lidong Guo3 and Zongbi Bao4,∗

1 Department of Physics, Naval Postgraduate School, Monterey, Ca 93943, United States of America
2 Department of Physics, The Hashemite University, Zarqa 13115, Jordan
3 Key Laboratory of Biomass Chemical Engineering of Ministry of Education, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, People’s Republic of China
4 Authors to whom any correspondence should be addressed.

E-mail: smalnemrat@hu.edu.jo and baozb@zju.edu.cn

Keywords: molecular dynamics, metal organic framework, density of state, bonding analysis

Supplementary material for this article is available online

Abstract

*Ab initio* Molecular Dynamic (MD) and static Density Functional Theory (DFT) are used to study the structural and bonding properties of small hydrocarbon adsorbates inside Ca(squarate)—Metal Organic Framework (MOF). Car—Parrinello Molecular Dynamics (CPMD) simulations of a single—adsorbate—MOF structure are used to obtain the adsorbate most preferred site of adsorption. This site is used for further structural and bonding analyses using static DFT. Unlike many other MOFs; we found that the Ca(squarate)—MOF physisorbs and weakly binds small adsorbate molecules such as C2H2, C2H4, C2H6, and C3H8 with no observed charge transfer and minimal hybridization with the MOF orbitals. No covalent bonding is seen near the preferred site of adsorption. The calculated binding energies decreases as the H content in the adsorbate molecule increases and found to be −18.71 kJ/mol, −18.14 kJ/mol, −15.75 kJ/mol, and −4.47 kJ/mol for C2H2, C2H4, C2H6, and C3H8 molecules respectively. Density of State (DOS) and a Crystal Orbital Overlap Population (COOP) analyses show that the interactions between C and H atoms in the molecule and C and O atoms in the MOF have antibonding characteristics near the Fermi level. These antibonding states tend to destabilize the overall electronic structure of the combined adsorbate/MOF system and hence decrease the binding energies of these adsorbates inside the MOF.

1. Introduction

Metal-Organic Frameworks (MOFs) are widely used for gas adsorption and separation applications[1–8]. These crystalline organic compounds are well-known for their exceptionally large pores and abilities to absorb and bind a wide range of molecules and ions. The ability to tune the organic linkers and/or metallic ion centers in MOFs results in a large collection of materials with unique properties [9–12]. MOFs, with appropriate organic/linker topologies, are widely used for molecular and ionic adsorption/separation applications [13–16]. Both processes are very important for several environmental and industrial applications such as carbon capturing, catalysis and energy storage [17–20]. MOFs with open-metal sites show high adsorption capabilities and strong bonding between between adsorbates and the metal centers inside the MOFs (depends on the metal type). Open metal site MOFs bind wide range of adsorbate molecules with varying binding energies from few kJ/mol to 100 kJ/mol [13]. However, packing large amount of gas into MOFs with this high adsorption/separation capabilities and high bonding energies required higher regeneration energy (effect seen in most open metal site MOF structures). Many adsorbents controlled parameters such as cost and efficiency are directly related to the regeneration process. For example; MOF’s half-life, quality, cost, and efficient adsorption capability necessitate a low regeneration energy [21, 22]. Recently, a calcium-based metal-organic (named Ca(squarate)) framework shows interesting high stability and high adsorption selectivities. This MOF is prepared using Calcium
Carbonate CaCO$_3$ and squaric acid [23, 24]. A square one dimensional channels are formed as a result of bonding between Ca$^{2+}$ ions and the squaric acid dianion (C$_4$O$_4^{2-}$) as shows in figure 1.

The measured diameters of these channels is 3.4 Å (Connolly radius of 1.0 Å) and with a nearly a perfect square pore area of 3.43.4 Å$^2$. Alongside its interesting topological features; the Ca(squarate) MOF exhibits a high thermo-stability and high adsorption selectivities for C$_2$H$_2$/C$_2$H$_4$ and C$_2$H$_4$/C$_2$H$_6$ separation. The experimental calculations of the isosteric heat of adsorption ($Q_{st}$) stands for stronger interactions between the adsorbate molecules and the MOF. The relationship between $Q_{st}$ and these interactions is evaluated by the separation performance of the Ca(squarate) MOF using breakthrough experiments of C$_2$H$_2$/C$_2$H$_4$ (50:50) and C$_2$H$_4$/C$_2$H$_6$ (50:50) mixtures at 298 K. These experiments have shown that the selectivity performance of Ca(squarate) MOF (8.1 and 5.9 C$_2$H$_2$/C$_2$H$_4$ (50:50) and C$_2$H$_4$/C$_2$H$_6$ (50:50) mixtures respectively) is high compared to many other known MOFs. [24]. Thermal-stability of MOF is very important for practical applications. The loading process of gas molecules inside the MOF can cause rapid temperature increase and hence desorption may take place during this process. In contrast to the many previously reported MOFs, the

---

**Figure 1.** 3 × 3 × 3 super cell of (a) side (b) top view of Ca(squarate) MOF. Gray: C, red: O, and cyan: Ca.
Ca(squarate) MOF shows significant adsorption ability and high chemical and thermal stability with efficient regeneration energy.

Deep understanding of bonding mechanism inside MOF is essential and can provide valuable information necessary for future tunable structures for practical applications. In this work we combined \textit{ab-initio} molecular dynamic simulations (MD) and static DFT calculations in order to explain the basic structural and bonding properties of small hydrocarbon molecules inside the degassed (water molecules are removed) Ca(squarate) MOF \cite{25-32}. The most preferable site of adsorption of adsorbate-MOF structure are obtained from MD simulations. A series of single-point energy calculations are carried out for adsorbate-MOF structure near their preferred site of adsorption. The most stable and preferred site of adsorption is used for further structural and bonding analyses using static DFT. We found that the Ca(squarate)-MOF physisorbs and weakly binds small hydrocarbon adsorbates considered in this study (\(\text{C}_2\text{H}_2\), \(\text{C}_2\text{H}_4\), \(\text{C}_2\text{H}_6\), and \(\text{C}_3\text{H}_8\)). No obvious charge transfer and minimal hybridization were observed between adsorbates and MOF orbitals. No covalent bonding is seen near the preferred site of adsorption. The calculated binding energies of \(\text{C}_2\text{H}_2\), \(\text{C}_2\text{H}_4\), \(\text{C}_2\text{H}_6\), and \(\text{C}_3\text{H}_8\) molecules inside this MOF are \(-18.71 \text{ kJ/mol}, -18.14 \text{ kJ/mol}, -15.75 \text{ kJ/mol}, \text{and} -4.47 \text{ kJ/mol}\) respectively. Density of State (DOS) and a Crystal Orbital Overlap Population (COOP) analyses, which is simply the DOS multiplied by the overlap population, are used to investigate the nature of bonding between these adsorbates and the MOF. COOP shows that the interactions between C and H atoms in the adsorbate and C and O atoms in the MOF’s have antibonding characteristics near the Fermi level. Although the summation of all interactions in the COOP plots is bonding in nature; the presence of these antibonding state tends to destabilize the overall electronic structure and hence decrease the binding energies of these adsorbates inside the MOF. The binding energies of all adsorbates with larger H content found to be less stable due to these antibonding states which are responsible for the low binding energies of these adsorbates inside the MOF. However, the physisorption nature of the these adsorbates has advantages, from industrial point of view, for efficient and reliable use of Ca(squarate)-MOF.

2. Computational details

\textit{Ab-initio} molecular dynamic and static calculations are performed on the Ca(squarate)-adsorbates combined systems. The original MOF, consists of 144 atoms, is fully optimized and set ready for MD simulations. A single adsorbate molecule (\(\text{C}_2\text{H}_2\), \(\text{C}_2\text{H}_4\), \(\text{C}_2\text{H}_6\), and \(\text{C}_3\text{H}_8\)) is inserted randomly inside the optimized MOF structure. Ab-initio MD within NVE ensemble is carried out for a total time of 3 ps for equilibration for each MOF-molecule structure. Following equilibration, an average MD run of 6 ps within NVT ensemble is carried out. Within NVT simulations, only the adsorbate molecules were allowed to evolve with time while the MOF atoms are constrained to their initially optimized and equilibrated geometries. Snapshots of the combined systems in all configurations were taken at the minimum potential energy profile by performing a series of single point energy calculations of large numbers of configurations near the MD preferred site of adsorption in order to identify the most stable structure. All configurations with a preferred adsorption sites inside the MOF are considered for the static ab-initio calculations for structural and bonding analyses. MD calculations were performed using a Car–Parrinello method as implemented in the CPMD code \cite{33}. Perdew–Burke–Ernzerhof (PBE) functional \cite{34} are used for the electronic ex-change and correlation effects. Norm-conserving Troullier-Martins pseudopotentials are used for the interactions between the nuclei and electrons with a plane wave basis set of cut-off energy of 140 Ry. Nose-Hoover thermostat is used to adjust the temperature during MD runs with a thermostat frequency of 2600 cm\(^{-1}\). A temperature of 1000 K is used to accelerate these dynamic calculations. The simulation time step used is 4 a.u. (0.097 fs) for the integration of equations of motion with a fictitious mass of 400 amu. Static DFT calculations were performed using the Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) \cite{35}. PBE are used for the exchange–correlation effects using the norm-conserving Troullier-Martins pseudopotentials. A cut-off energy of 240 Ry was used for the expansion of the band states. A k-grid cut-off radius scheme of 16 Å–point sampling of the Brillouin zone was used. A double-zeta plus polarization (DZP) basis set was used for the expansion of the electronic wavefunctions. Convergence is achieved as the forces and total energy per atom were less than 50 meV/Å and 3 meV, respectively. Non-spin achieved with no thermal corrections were employed in these calculations. All static calculations were carried out at 0 K. COOP analysis, which sums over all possible overlap states, was performed to distinguish bonding and antibonding orbital interactions between adsorbate and MOF atoms. Although we are studying the degassed MOF in which all water molecules are removed; we extended these simulations using the same computational methodology to study the effect of possibly having water molecules attached to Ca inside the MOF on the the bonding energies of all adsorbates as will be discussed in the next section.
3. MD simulations

We first present ab initio MD of each adsorbate-MOF system. An adsorbate molecule is placed randomly inside the MOF with the constraint that all atoms of the adsorbate molecules should start no closer than 2 Å from the MOF. The MOF atoms are held fixed and ≈ 6 ps NVT simulations are started following the initial equilibration. Initial molecular dynamics simulations with a single adsorbate showed that the adsorbate molecules performed random rotations and fluctuations inside the MOF and getting closer to the squarate ring in the MOF. Snapshots of the final configurations of all adsorbate-MOF structures at the end of NVT-MD simulations are shown in figure 2.

MD simulations showed that (after ≈ 2 ps of simulation time) the C-H bond is slightly distorted. As the simulations evolved, C₂H₂ and C₂H₆ molecules found to have a nearly perfect vertical configuration with a nearest neighbor separation distances between the carbon atoms in the adsorbate molecules and the carbon atoms in the MOF are 2.52 and 2.45 Å, respectively. This configuration found to be stable and last to the end of the NVT-MD simulations. On the other hand, C₂H₄ and C₃H₈ relaxed in a planar configuration with a nearest neighbor separation distance between the carbon atoms in the adsorbate molecules and the carbon atoms of the MOF of ≈ 2.60 Å. The bond distributions as the probability of finding specific bonds within a cut-off radius of 3.0 Å are averaged along MD trajectories and shown in the corresponding Pair Distribution Functions (PDF) in figure 3.

Figure 2. Final configuration of (a) C₂H₂ (b) C₂H₄ (c) C₂H₆ and (d) C₃H₈ inside Ca(squarate) MOF at the end of NVT-MD simulations. Gray: C, red: O, white: H, and cyan: Ca.
at larger distances of ≈ 4.20 and 5.30 Å. The highest probable O-C bond distribution is seen at 1.26 Å and is due C-O bonds of the squarate acid (figure 3(b)). Lower C-O bond distribution probabilities are observed at 2.50 and 3.50 Å which include bonds between C atoms in the adsorbate molecules and O atoms in the MOF. Also, C-H and O-H PDFs are shown in figures 3(c) and 3d respectively. These bond distributions are specific for bond distributions of H atoms in the adsorbate molecules and the C and O atoms in the MOF. The first peak in the C-H bonds distribution is localized at ≈ 1.10 Å which is the equilibrium C-H bond within the adsorbate molecule itself. The second peak at 2.50 Å is due H-C bonds between H atoms in the adsorbate and C atoms in the MOF. Finally, H-O bond distributions are observed at distances beyond 2.0 Å for all adsorbate-MOF structures.

Analysis of the effective diffusion constant based on the Mean Square Displacement (MSD) for C₂H₂ and C₃H₈ species inside the MOF is shown in figure S1 of supplementary information (SI) available online at stacks.iop.org/JPCO/6/045001/mmedia. Einstein relation [36] is used to roughly estimate the self-diffusion coefficients based on the MSD as a function of simulation time. The calculated diffusion constants of C₂H₂ and C₃H₈ inside the MOF are 1.16 and 2.54 × 10⁻⁹ m²/s respectively. We believe that our estimates, within the simulation time considered here, are not reliable to establish accurate diffusion measurements, however, this is useful fast metric for comparison the calculated binding energies as we will discuss in the next section. At the beginning of these simulations, both C₂H₂ and C₃H₈ have nearly the same MSD as a function of time. After the first 3 ps, C₃H₈ has larger MSD than that of C₂H₂ and can be explained in terms of its calculated binding energy which is found less than that of C₂H₂. Although, the binding behavior between the adsorbed molecules and the MOF is nearly identical for all adsorbates considered in this study, the variation in the calculated binding energies will be explained in terms of bonding/antibonding characteristics between adsorbates and MOF atoms.

4. Binding energies

The most stable configuration of all adsorbates inside the MOF following the NVT-MD simulations are used for our binding energies calculations. Figure 4 and table 1 summarize some structural measurements of the optimized structures used in these calculations.

We calculated the binding energy of each adsorbate inside the MOF using the relation $E_b = E_{\text{comb}} - E_{\text{MOF}} - E_{\text{molecule}}$. Where $E_b$ is the calculated binding energy, $E_{\text{comb}}$ is the total energy of the combined system (adsorbate + MOF), $E_{\text{MOF}}$ is the total energy of the base MOF, and $E_{\text{molecule}}$ is the total energy of the isolated adsorbate. The calculated binding energies of C₂H₂, C₂H₄, C₃H₆, and C₃H₈ inside the MOF are −18.71 kJ/mol, −18.14 kJ/mol, −15.75 kJ/mol, and −4.47 kJ/mol respectively (negative sign means favorable binding). Mulliken population analysis of the charge density (figure 5) shows that there is small charge transfer between the adsorbate molecules and the MOF and supports our findings on the calculated binding energies.
The experimentally calculated isosteric heat of adsorption ($Q_{st}$) for $\text{C}_2\text{H}_2$, $\text{C}_2\text{H}_4$, and $\text{C}_2\text{H}_6$ adsorbates are 37.6 kJ/mol, 33.9 kJ/mol, and 28.4 kJ/mol, respectively. Higher $Q_{st}$ values stands for stronger interactions between the adsorbate molecules and the MOF. The relationship between the $Q_{st}$ and the interaction between the adsorbate molecules and the adsorbent is evaluated by the separation performance of the Ca(squarate) MOF using breakthrough experiments of $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ (50:50) and $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ (50:50) mixtures at 298 K. In $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ experiment, the interaction between $\text{C}_2\text{H}_4$ and the framework is found weaker than that of $\text{C}_2\text{H}_2$ which is found to reach saturation much slower than $\text{C}_2\text{H}_4$. The same observations are confirmed for the other $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ mixture. Based on these measurements, the binding energies of the $\text{C}_3\text{H}_8$ molecule, considered in our calculations but not the experiment, is expected to have less binding energy inside the MOF and this what we predicted theoretically. These calculations alongside the experimental measurements confirms that this MOF is a promising material for separation of these molecules. Although our calculated binding energies are close to the measured $Q_{st}$, the measured $Q_{st}$ are based on the Clausius-Clapeyron equation which is a function of real temperatures and pressures. However, the hierarchy of these energies are in good agreement with the previously reported experimental isosteric heat of adsorption [24]. Although we are interested in the degassed MOF in which all water molecules are removed; the effect of water remnant inside the simulation cell is investigated. The possibility of having water molecules inside the MOF found to increase the binding energies of all adsorbates by $\approx 3$ to $8$ kJ/mol. H atoms in the adsorbate molecules form positive bonding with O atoms in the water molecules inside the MOF. These interactions increase the binding energies as will be discussed in more details in terms of COOP analysis in the next section. However, these binding energies confirm the ability of this MOF to physically host these adsorbates with relatively small regeneration energy, and this is of particular industrial interests in terms of MOF ‘s reliability, quality and cost.

Table 1. Structural measurements of the optimized MOF and MOF with adsorbate molecules taken at the end of the MD simulations (average nearest neighbor bond lengths only included). $\text{C}_{\text{ads}}$ means C atoms in the adsorbate molecule and $\text{C}_{\text{MOF}}$ means carbon atom in the MOF structure.

| Adsorbate-MOF   | $\text{Ca-C}_{\text{ads}}$ (Å) | $\text{Ca-O}$ (Å) | $\text{Ca-C}_{\text{MOF}}$ (Å) | $\text{C-C}_{\text{ads}}$ (Å) | $\text{C-C}_{\text{MOF}}$ (Å) | $\text{C-O}_{\text{ads}}$ (Å) | $\text{C-O}_{\text{MOF}}$ (Å) |
|-----------------|-------------------------------|-------------------|-------------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| $\text{C}_2\text{H}_2$-MOF | 1.26                          | 2.52              | 3.30                          | 1.47                        | 2.51                        | 1.26                        | 3.22                        |
| $\text{C}_2\text{H}_4$-MOF | 1.35                          | 2.64              | 2.85                          | 2.31                        | 2.31                        | 2.48                        | 3.02                        |
| $\text{C}_2\text{H}_6$-MOF | 1.42                          | 2.45              | 3.20                          | 1.85                        | 1.85                        | 1.93                        | 3.08                        |
| $\text{C}_3\text{H}_8$-MOF | 1.55                          | 2.61              | 2.54                          | 1.72                        | 1.72                        | 1.55                        | 3.02                        |
5. Density of States

The Density of State (DOS) and Partial Density of States (PDOS) of the isolated C$_2$H$_2$ molecule and inside the MOF are shown in figure 6.

All occupied states arise mainly from C-O orbitals. These C-O interactions are almost entirely bonding in character and arise from a combination of C$_{2p}$-O$_{2p}$, C$_{2s}$-O$_{2p}$, and C$_{2p}$-O$_{2s}$ hybridizations occupying all states below the Fermi level up to -11.0 eV with smaller contributions from Ca/H atoms. The inset of figure 6 shows the contribution from C and H atoms of C$_2$H$_2$ molecule to the total DOS. Pure C$_{2p}$ states localized around -2.0 eV and C$_{2p}$-H$_{1s}$ hybrid states appeared at -8.0 and -10.0 eV. The H contribution to the total DOS is more dominant in other molecules that contain more H atoms as shows in figure 7 for C$_3$H$_8$ molecule inside the MOF.

No pure C-state appeared in the C$_3$H$_8$ molecular DOS. However, strong C$_{2p}$-H$_{1s}$ hybridization clearly appeared in the entire region below the Fermi level. DOS of state of C$_3$H$_8$ inside the MOF has similar characteristic to the DOS of C$_2$H$_2$ inside the MOF with larger contributions from H atoms. In the latter case, pure H states can be seen deep at -12.0 eV. The total DOS and molecular DOS of remaining C$_2$H$_4$/MOF systems are shown in figure S2 in SI file. DOS provides valuable information on the occupied states of adsorbates and MOF atoms. However, the nature of bonding between these atoms can’t be obtained from DOS. In order to explain the variation in the binding energies of these adsorbates inside the MOF in terms of their interactions; Crystal Orbital Overlap Population (COOP) analysis is performed. COOP are simply the DOS multiplied by the overlap population which provide information on the bonding nature between the electronic states in the DOS plots. COOP allows distinguishing between bonding, anti-bonding, and non-bonding orbital interactions, depending on the sign of the overlap matrix between electronic states. This is useful for searching of new states near the Fermi level and the effect of these states on the overall electronic structure. Bonding orbitals appear with positive overlap matrix elements, anti-bonding orbitals appear with a negative sign, and non-bonding orbitals appear with zero element in the overlap matrix element. In all COOP analyses; we consider interactions between C and H atoms in the adsorbate molecules and C and O atoms in the MOF within a cut off distance of 3.0 Å. No interactions beyond this cut-off is taken into account in these calculations. Figure 8 shows details of COOP plot of C$_2$H$_2$ molecule inside the MOF.
Figure 6. DOS and PDOS of the isolated C₂H₂ molecule and inside the MOF.

Figure 7. DOS and PDOS of the isolated C₃H₈ molecule and inside the MOF.
Overall, all interactions have a positive bonding characteristic over a wide energy range from $-4.30$ to $-14.0$ eV. These states are mainly $C_2p-C_2p$ and hybrid $C_2p-O_2p$ states. However, these C-C interactions in this system show a clear antibonding characteristic closer to the Fermi energy at $\approx -1.5$ and $-3.0$ eV. The same characteristics appeared in the H-O interactions (figure 8(b)). Mixed $H_1s-O_2p$ and $H_1s-O_2s$ antibonding states near the Fermi level are observed at the same energy levels at $-1.50$ and $-3.0$ eV. In contrast, H-C COOP shows minimal antibonding characteristics around $-2.50$ eV. The summation of all these interactions between the adsorbate and the MOF is positive (a stable molecular structure and preferable adsorption mechanism). However, the presence of these antibonding states near the Fermi level tends to destabilize the overall bonding nature between $C_2H_2$ adsorbate and the MOF. Hence, the binding energy decreases as a result of these antibonding interactions. C-C COOP curves are consistent for other adsorbates with stronger bonding/antibonding states as the number of H atoms increases in each adsorbate (figures S3, S4, and S5 in SI). Other H-C and H-O COOP curves of all other adsorbates have the same characteristics where several antibonding states appeared near the Fermi level and hence have the same destabilization effect on the bonding nature of these adsorbates inside the MOF. The overall C-C, H-C, and H-O interactions are bonding in nature but with significant anti-bonding contributions. The origin of these anti-bonding states is mainly $C_2p-C_2p$, $C_2p-O_2p$, and

Figure 8. COOP of (a) C-C (b) H-O and (c) H-C between $C_2H_2$ and MOF.
H$_1$-C$_{2p}$ with smaller contributions from C$_{2s}$-C$_{2p}$ and C$_{2s}$-O$_{2s}$ hybridizations. The present of water molecules inside the MOF added more interaction possibilities between the adsorbate atoms and the water molecules. We found that the binding energy of adsorbates and MOF with H$_2$O molecules attached to Ca atoms has slightly increased the binding energies by $\approx 3$–8 kJ/mol for all adsorbates. The increase in the binding energies is attributed to the positive bonding between the H atoms in the adsorbate molecules and O atoms from the water molecules. The H-O COOP and DOS plots of C$_2$H$_2$ inside the MOF with at least one water molecule attached to each Ca atom in the MOF is shown in figure 9. The amount of positive bonding between H and O orbitals increases and the amount of antibonding states decreases (y-axis of figure 9) compared to the previously discussed case with no water molecules present inside the simulation cell (figure 8(b)). The main features in the COOP is nearly unchanged except the amount of bonding/antibonding states between H and O atoms. COOP analyses presented in these calculations confirm the physical adsorption capability of this MOF in terms of these bonding/antibonding states near the Fermi level, in which the antibonding states tend to destabilize the overall adsorption mechanism of these adsorbates and lower their binding energies inside this MOF.

6. Conclusion

We combined ab-initio molecular dynamic and static density functional theory are used to study the structural and bonding properties of small hydrocarbon adsorbates inside Ca(squarate)-Metal Organic Framework (MOF). We found that the Ca(squarate)-MOF physisorbs and weakly binds small adsorbate molecules such as (C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$, and C$_3$H$_8$) with no observed charge transfer and minimal hybridization with MOF’s atoms. The calculated binding energies of C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$, and C$_3$H$_8$ inside the MOF were $-18.71$ kJ/mol,

Figure 9. (a) COOP of H-O interactions and (b) total DOS of C$_2$H$_2$ and MOF with water molecules intact to the Ca ions inside the MOF.
−18.14 kJ/mol, −15.75 kJ/mol, and −4.47 kJ/mol respectively. DOS and COOP analyses provide information on the bonding nature between the adsorbate and MOF. COOP shows that the interactions between adsorbate carbon and H atoms with the MOF’s C and O atoms have antibonding characteristic near the Fermi level. The presence of these antibonding state tends to destabilize the overall electronic structure and hence decrease the binding energies of these adsorbates inside the MOF. Finally, we investigated the possibility to have water molecules inside the MOF and found that the binding energies of these adsorbates increased by by ≈3−8 kJ/mol as a result of positive bonding between the H atoms in the adsorbate and O atoms from the water.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

ORCID iDs

Sufian Alnemrat https://orcid.org/0000-0002-5143-4066

References

[1] Xiang W, Zhang Y, Chen Y, Liu C and Tu X 2020 J. Materials Chemistry A 8 21526−46
[2] Furukawa H, Cordova K E, O’Keeffe M and Yaghi O M 2013 Science 341 1230444
[3] Jingui D, Yiichang P, Gongping L and Wanchin J 2018 Curr. Op. Chem. Eng. 20 122−31
[4] Gao J, Qian X, Lin R, Krishna R, Wu H, Zhou W and Chen B 2020 Angew. Chem. Int. Ed. 59 4396−400
[5] Zhou H and Kitagawa S 2014 Chem. Soc. Rev. 43 5415−8
[6] Lee Y, Kim J and Ahn W 2013 Korean J. Chem. Eng. 30 1667−80
[7] James S L 2003 Chem. Soc. Rev. 32 276−88
[8] Yuan Set al 2018 Adv. Mater. 30 1704303
[9] Tan K, Zuluaga S, Fuentes E, Mattson E C, Veyan J, Wang H, Li J, Thonhauser T and Chabal Y J 2016 Nature Communication 17 13871
[10] Ding M, Flaig R W, Jiang H and Yaghi O M 2019 Chem. Soc. Rev. 48 2783−828
[11] Sirca S 2001 Adsorption Science & Technology 19 347−66
[12] Demir H and Keskin S 2021 Molecular Systems Design & Engineering 6 627−42
[13] You W, Liu Y, Howe J D and Sholl D S 2018 J. Phys. Chem. C 122 8960−6
[14] Bao Z, Yu L, Dou T, Gong Y, Zhang Q, Ren Q, Lu X and Deng S 2011 J. Chem. & Eng. Data 56 6017−23
[15] Bao Z, Alnemrat S, Yu L, Vasiliev I, Ren Q, Lu X and Deng S 2011 Langmuir 27 13554−62
[16] Gautam S and Cole D 2020 Nanomaterials 10 2274
[17] You W, Liu Y, Howe J D, Tang D and Sholl D S 2018 J. Phys. Chem. C 122 8960−6
[18] Liu W, Yin R, Xu X, Zhang L, Shi W and Cao X 2019 Advanced Science 6 1802373
[19] Zheng J, Vemuri R S, Estevez L, Koehl P K, Varga T, Camaioni D M, Blake T A, McGrail B P and Motkuri R K 2017 J. American Chemical Society 139 10601−4
[20] Shinzawa H, Bayer B C, Peterlik H, Meyer J C, Lang W and Pichler T 2017 Sci. Rep. 7 2439
[21] Britt D, Furukawa H, Wang B, Glover G, Yaghi O M and Halpern J 2009 Proceedings National Academy of Sciences of the USA 106 20637−40
[22] Sadig M M, Konstas K, Falcaro P, Hill A J, Suzuki K and Hill M R 2020 Cell Reports Physical Science 1 100070
[23] Lin R, Li L, Zhou H, Wu H, He C, Li S, Krishna R, Li J, Zhou W and Chen B 2018 Nat. Mater. 17 1128−33
[24] Li L, Guo L, Pu S, Wang J, Yang Q, Zhang Z, Yang Y, Ren Q, Alnemrat S and Bao Z 2019 Chem. Eng. J. 358 446−55
[25] Sun Y Y, Lee K, Kim Y and Zhang S B 2009 Appl. Phys. Lett. 93 033109
[26] De Oliveira A, De Lima G F and De Abreu H A 2018 Chem. Phys. Lett. 691 283−90
[27] Shen Y et al 2021 App. Phys. Rev. 8 031411
[28] Lee K, Howe J D, Lin L, Smit B and Neaton J B 2015 Chem. Mater. 27 668−78
[29] Rudenko A N, Bendt S and Kell F J 2014 J. Phys. Chem. C 118 16218−27
[30] Tao S, Manquan F, Zhen W, Lixin Y and Hiding L 2017 Modelling Simul. Mater. Sci. Eng. 25 35002−15
[31] Hermann H, Elsner A and Stoyan D 2013 Modelling Simul. Mater. Sci. Eng. 21 85005−22
[32] Mattesini M, Soler J M and Yndurain F 2006 Phys. Rev. B 73 094111−9
[33] Hutter J 2012 WIREs Comput. Mol. Sci. 2 694−12
[34] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865−8
[35] Soler J M, Artacho E, Gale J D, Garcia A, Junquera J, Ordejón P and Sánchez-Portal D 2002 J. Phys.: Cond. Matt. 14 2745−79
[36] Pekka M and Lennart N 2001 J. Phys. Chem. A 105 9954−60