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ARTICLE *in* JOURNAL OF PHYSICAL CHEMISTRY LETTERS · JUNE 2010

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Adsorption Sites and Binding Nature of CO₂ in Prototypical Metal–Organic Frameworks: A Combined Neutron Diffraction and First-Principles Study

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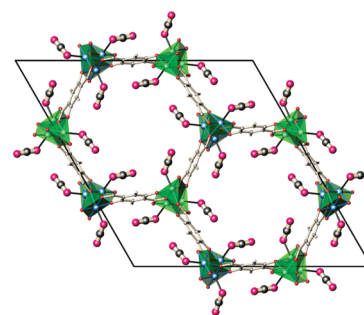
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ABSTRACT We report a detailed study of CO₂ adsorption in two important metal–organic framework (MOF) compounds (Mg-MOF-74 and HKUST-1). In both MOFs, the open metal ions were identified as the primary binding sites through neutron diffraction measurements. The relatively strong metal–CO₂ binding was attributed to an enhanced electrostatic interaction, and vibrational mode analysis shows that the adsorbed CO₂ molecule is strongly attached through one of its oxygen atoms while the rest of the molecule is relatively free. This high orientational disorder is the reason for the large apparent O–C–O bond bending angle derived from diffraction measurements. Our calculations give only a small degree of bond bending, suggesting that the CO₂ adsorption on the open metal site is still largely physisorption. Interestingly, the overall metal–CO₂ binding strength is right in the range which can facilitate both adsorption (CO₂ capture) and desorption (MOF regeneration) under typical flue gas conditions.

SECTION Surfaces, Interfaces, Catalysis



Capture of CO₂ from industrial flue gas and the subsequent storage of CO₂ have attracted intensive research interests in recent years because of their significant environmental implications. Among various methods investigated, material-based CO₂ adsorption has emerged as a promising route. In particular, metal–organic frameworks (MOFs), a relatively new family of nanoporous materials, have exhibited great promise for CO₂ separation and storage.^{1,2} Determining where the CO₂ molecules are actually adsorbed in these MOF compounds, and the corresponding adsorption mechanisms would provide key guidance for further rational development of new MOF materials tailored toward improved CO₂ adsorption and separation. Thus far, structural studies of the CO₂ locations have been only reported for a few MOF systems (MIL-53, Ni-MOF-74, etc.),^{3–6} mainly using X-ray diffraction methods; however, detailed analysis of the CO₂ binding mechanism is scarce.

Here, we report a combined neutron diffraction and first-principles study on the CO₂ adsorption in two important prototypical MOF compounds, Mg-MOF-74 [Mg₂(dobdc), dobdc = 2,5-dioxido-1,4-benzene-dicarboxylate; also known as CPO-27-Mg or Mg₂(dhtp)] and HKUST-1 [Cu₃(btc)₂, btc = 1,3,5-benzenetricarboxylate]. Mg-MOF-74 was previously reported to exhibit exceptionally high CO₂ adsorption enthalpy⁷ and good CO₂ separation capacity,⁸ while HKUST-1 is one of the most widely studied MOF compounds and is often used as a benchmark material.⁹ Structurally, both MOFs contain open metal sites that are known to play a vital role in enhanced binding of various gas molecules (H₂, CH₄, C₂H₂, NO, etc.).^{10–16}

It would thus be interesting to see whether these open metal sites may dominate the CO₂ adsorption as well. The pore structure of Mg-MOF-74 is one-dimensional channel-like, with a nominal diameter of ~13 Å. HKUST-1 has a more complicated pore structure, containing three types of cage-like pores. The small pore has a dimension of ~4 Å, while the two large ones are ~10 and ~11 Å, respectively. These pores with various sizes in HKUST-1 provide an opportunity to investigate how pore geometry may influence the CO₂ affinity.

Mg-MOF-74 and HKUST-1 samples were synthesized using the solvothermal methods following recipes reported previously.^{7,11} Samples were then fully activated at elevated temperature in a dynamic vacuum (HKUST-1: at 423 K for 24 h; Mg-MOF-74: at 473 K for 72 h). Neutron powder diffraction measurements were performed using the high-resolution neutron powder diffractometer (BT-1) at the NIST Center for Neutron Research. Data were first collected on a bare MOF sample at 20 K to confirm the full activation of the material. The sample was then warmed to ~240 K, and various known amounts of CO₂ were loaded into the MOF sample using a Sievert-type apparatus. Afterward, the sample was slowly cooled to ~196 K (in about 1 h), at which point the pressure decreased to a negligible value as the CO₂ was completely

Received Date: May 1, 2010

Accepted Date: June 3, 2010

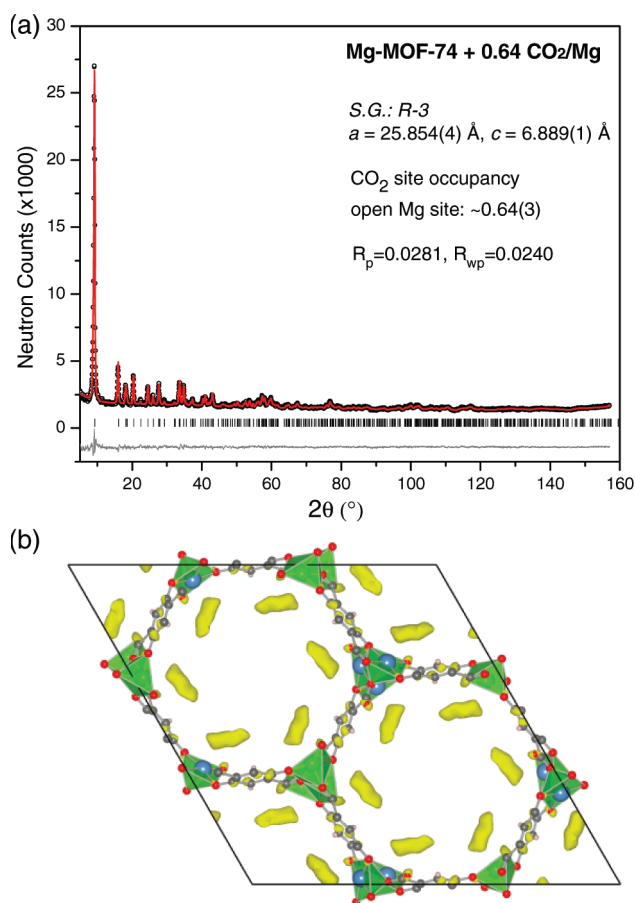


Figure 1. (a) Observed (dots), refined (line), and difference (noisy line) neutron powder diffraction profiles of the Mg-MOF-74 sample with adsorbed CO₂. Crystal unit cell parameters, CO₂ occupancies, and goodness of fit are shown in the inset. (b) Real space Fourier difference scattering length density (yellow regions) superimposed on the Mg-MOF-74 structure (color scheme of atoms: Mg, blue; C, gray; O, red; and H, white), clearly indicating that the adsorbed CO₂ is located on top of the open Mg ions.

adsorbed. The sample was further cooled to 20 K for diffraction data collection. Rietveld structural refinements were done using the GSAS package.¹⁷ No evidence of solid CO₂ was observed in the structural refinement of the CO₂ loaded samples, indicating that all CO₂ was adsorbed into the MOF structure. The CO₂ concentrations derived from structural refinement agree well with the experimental loading calculated from gas amount and sample mass, and thus in the following, we simply use the refined CO₂/open-metal ratio to denote the CO₂ concentrations in our MOF samples.

The observed and refined neutron diffraction profiles of the Mg-MOF-74 sample with a CO₂ loading of 0.64 CO₂/Mg are shown in Figure 1a [those of the bare Mg-MOF-74 sample are shown in the Supporting Information (SI, Figure S1)]. Using the Fourier difference technique,^{18–21} we were able to unambiguously identify the location and orientation of the adsorbed CO₂ molecules (see Figure 1b), which we followed with a full-profile Rietveld refinement, resulting in an excellent fit. The goodness of fit and site occupancies are shown in the inset of Figure 1a, while detailed information of refined

CO₂ coordinates can be found in the SI (Table S1). For the 0.64 CO₂/Mg loading, all CO₂ molecules go to the open Mg site, as expected. We did not perform more measurements at higher CO₂ loadings because the framework pore surface would have been largely coated once the open Mg sites were fully occupied, and thus, any additional sites populated at high CO₂ concentration would not have been typical monolayer surface adsorption sites. The primary CO₂ adsorption on the open metal identified here is also in general agreement with that found previously⁶ in Ni-MOF-74 by Dietzel et al. using X-ray diffraction. This is not surprising since Mg-MOF-74 is isostructural to Ni-MOF-74, and previous isotherm measurements⁷ showed that the CO₂ adsorption enthalpy on Mg is similar to, though even larger than, that on Ni. Somewhat unexpected is that the refined O–C–O bond angle of the CO₂ adsorbed on open Mg is ~160.5°; a similar bond angle of 162° was reported⁶ for CO₂ in Ni-MOF-74. This distortion is unexpected for a linear molecule such as CO₂, and such a large degree of bond bending would indicate that the metal–CO₂ interaction is strong enough to result in significant CO₂ bond activation. This behavior would be quite unusual for reversible physisorptive binding. However, as we will discuss in detail later, the actual bond angle is much smaller than is indicated by refinements due to disorder that originates from a very large anisotropic orientational potential of CO₂ on metal sites.

We show in Figure 2a and b the observed and refined neutron diffraction profiles of the HKUST-1 sample with adsorbed CO₂ (those of the bare HKUST-1 sample are shown in SI Figure S2). Data were collected for two different CO₂ loadings (1.07 and 1.47 CO₂/Cu) to locate all surface sites. From the Fourier difference maps (Figure 2c), two primary adsorption sites are clearly identified. One is the open Cu site, while the other is what we call the small cage window site, where the CO₂ sits in the four triangular-shaped openings into the small octahedral cage. Interestingly, although each open Cu site can only accommodate one CO₂, the molecule may orient in four possible directions, with one end O atom affixed to Cu. This was modeled using two independent sets of CO₂ molecular coordinates, each of which generates an equivalent CO₂ molecule on each Cu ion due to the mirror plane under the *Fm* $\bar{3}$ *m* space group symmetry. All other CO₂ adsorption sites are well-described by a single set of molecular coordinates. Full-profile Rietveld refinements were performed, and the fits are again excellent. The goodness of fit and site occupancies are provided in the inset of Figure 2a and b, while refined CO₂ coordinates are included in SI (Tables S2 and S3). As expected, at low CO₂ concentration, most CO₂ molecules go to the open Cu sites. Only at high loading is there a significant amount of CO₂ found on the small cage window site, as well as a small amount at two secondary adsorption sites (i.e., the center of the small octahedral cage and the corner of the large cuboctahedral cage, named small cage center site and large cage corner site, respectively; see Figure S3 in SI). These findings are similar to previous studies on the adsorption of other small gas molecules (e.g., H₂, CH₄, and C₂H₂) in HKUST-1,^{14,15,22} where the open Cu sites were found to be the strongest binding site, and other sites only were populated after the Cu sites had nearly full occupancy.

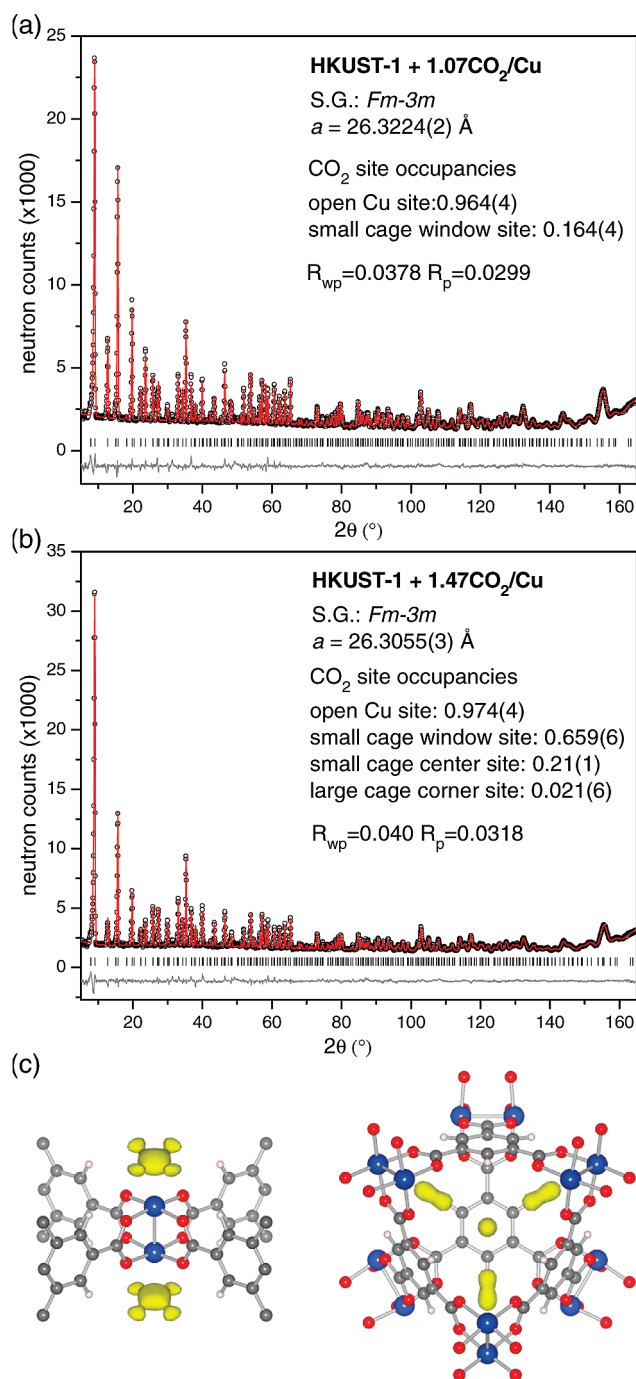


Figure 2. (a, b) Observed (dots), refined (line), and difference (noisy line) neutron powder diffraction profiles of the HKUST-1 sample with two different loadings of adsorbed CO₂. Crystal unit cell parameters, CO₂ occupancies, and goodness of fit are shown in the inset. (c) Real space Fourier difference scattering length density (yellow regions) superimposed with the partial structure of HKUST-1 (color scheme of atoms: Cu, blue; C, gray; O, red; and H, white), clearly indicating that the adsorbed CO₂ is primarily located on top of the open Cu ions (left) and the window opening of the small octahedral cage (right).

With the above structural information on CO₂ adsorption available, we can now discuss the nature of the adsorption in these two prototypical MOFs. For adsorption sites other than

the open metal sites, the framework–CO₂ interaction is mainly of van der Waals (vdW) type, though the binding strength could vary depending on the shape of the local vdW surface. Just as what we found previously for other gas molecules, accessible small cages and channels often generate pockets of enhanced adsorption potential, in which the total vdW interaction is relatively strong due to the gas molecule interacting with multiple “surfaces”.²² The CO₂ adsorption at the small cage window site in HKUST-1 is a good example of this; the triangular-shaped window opening of the small octahedral cage forms a narrow vdW potential well, into which a linear CO₂ molecule fits nicely, and consequently, the interaction strength is relatively large. For CO₂ adsorption on the open metal sites, the binding is clearly stronger than a typical vdW interaction, as evidenced by the fact that CO₂ is almost exclusively populated on the open metal sites at low CO₂ concentration in both Mg-MOF-74 and HKUST-1. The enhanced overall binding presumably originates from the strong electrostatic interaction between the open metal ion and the CO₂ quadrupole moment.

To further clarify the nature of this enhanced metal–CO₂ interaction, we performed first-principles calculations based on density functional theory (DFT).^{23,24} The calculated static binding energies of CO₂ derived from the local density approximation (LDA) and the generalized gradient approximation (GGA) are 51.2 and 20.2 kJ/mol for open Mg and 32.7 and 7.3 kJ/mol for open Cu, respectively. As expected, LDA overestimates the binding strength, while GGA underestimates it. Nevertheless, the relative binding strengths of open Mg versus those of open Cu derived from the two are consistent with previous experimental heat of adsorption measurements.⁷ In terms of the magnitude, the calculated binding strengths are still well within the regime of physisorption, although toward the high end. The enhanced binding energy perturbs the C–O bond lengths upon adsorption, with the C–O bond pointing to the open metal becoming elongated by ~1 % (compared with that of free CO₂) while the other C–O bond is contracted by ~0.5 %. Further inspection of the electron density and projected charges reveals that the charge distribution of the adsorbed CO₂ is also slightly redistributed. Due to the enhanced metal–CO₂ interaction, one may expect the CO₂ molecule to be slightly polarized or even bent. Indeed, the bond angles derived from our DFT calculations suggest a noticeable bond bending. The calculated O–C–O bond angles from LDA and GGA are 175.0 and 178.6° for the CO₂ on open Mg and 178.7 and 179.4° for the CO₂ on open Cu. Note, however, that the degree of bond bending calculated here is significantly smaller than that derived from our neutron diffraction data refinement. The origin of this difference will be addressed shortly. All of these observations suggest that upon adsorption on the open metal ion, multipole moments are induced to the CO₂ molecule, which would interact effectively with the open metal and lead to enhanced overall binding. Comparing open Mg and open Cu, the CO₂ on Mg was polarized more than that on Cu, in accord with the stronger binding strength of the former.

Next, we discuss the vibrational modes of adsorbed CO₂ molecules, which can give further information on the strength and shape of the local potential at the adsorption site. Also, the

Table 1. Vibrational Mode Energies (unit, meV) of Adsorbed CO₂ on the Open Metal Sites and Free CO₂ Molecule, Derived from DFT-LDA Calculations (1 meV = 8.066 cm⁻¹)

	CO ₂ on open Mg (in Mg-MOF-74)	CO ₂ on open Cu (in HKUST-1)	free CO ₂
C–O asymmetric stretching mode	300.0	299.4	301.6
C–O symmetric stretching mode	166.1	166.3	167.6
O–C–O bending modes	70.4, 76.1	76.4, 77.5	79.8, 79.8
additional modes	4.3, 8.5, 12.2, 15.6, 21.3	0.2, 3.4, 11.1, 11.1, 19.1	

modes can be easily probed by various experimental techniques (IR, Raman, or neutron spectroscopy). A free CO₂ molecule has four well-known vibrational modes,²⁵ one asymmetric stretching mode (2349 cm⁻¹/291.2 meV, IR active), one symmetric stretching mode (1333 cm⁻¹/165.3 meV, Raman active), and two degenerate orthogonal O–C–O bending modes (667 cm⁻¹/82.7 meV, IR active). Our DFT-LDA calculation on a free CO₂ molecule produces vibrational frequencies (see Table 1) reasonably close to the above-mentioned experimental values. We then performed phonon calculations of the CO₂ molecules adsorbed on the open metal sites in MOFs, assuming a rigid MOF host framework. As shown in Table 1, upon the adsorption on the open metal site, all four vibrational modes present in free CO₂ exhibit a softening, that is, a red shift of the peak position in the vibrational spectrum. In particular, the O–C–O bending modes (with degeneracy lifted upon CO₂ adsorption) exhibit a relatively large softening, and the magnitude clearly correlates with the CO₂ adsorption affinity. There are also five additional vibrational modes in the low-energy range, corresponding to CO₂ vibrating as a whole with respect to the open metal. These modes reflect how the potential at particular adsorption sites (i.e., the local potential being shallow or deep) affects the CO₂ position, orientation, and molecular motion. A few of these modes have rather low frequencies (see Figure 3a and b) and thus can be easily populated even at relatively low temperature, leading to some degree of disorder of the CO₂ position/orientation that would appear in the diffraction data. In general, the degree of the disorder increases with increasing temperature. At very low temperature, the CO₂ disorder is mainly a static one, while at elevated temperature, the CO₂ becomes mobile with its various phonon modes getting thermally excited, and the disorder changes into mainly a dynamic one. Interestingly, the CO₂ in HKUST-1 has one mode with nearly zero energy, suggesting large freedom of the adsorbed CO₂ vibrating along that particular direction. To gain more direct information about the CO₂ “mobility”, we performed frozen phonon calculations on the two representative CO₂ motions in HKUST-1 that are shown in Figure 3b. The potential energy was then plotted as a function of CO₂ rotational angle (see Figure 3c). As expected, the energy curves are rather shallow, particularly in the ±10° region, allowing for significant disorder with little effect on the total energy of the system. These findings are in excellent agreement with the relatively large thermal parameters of CO₂ adsorbed on the open metal sites, HKUST-1 in particular, that were obtained from the neutron diffraction refinement (see SI Table S2 and S3). It also answers the above-mentioned bond angle puzzle. The presence of disorder (either static or dynamic) in the orientation of the CO₂ molecule causes the

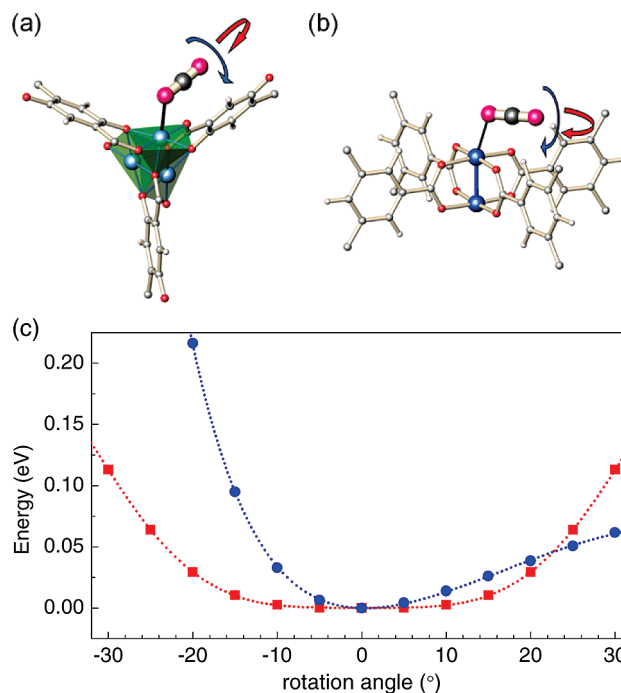


Figure 3. (a, b) Schematic showing the two lowest-energy vibrational/rotational modes of CO₂ in Mg-MOF-74 and HKUST-1. The O bound to the open metal is nearly fixed and can be approximated as the rotational center. In both MOFs, the open metal and the associated carboxyls from the ligands form a nearly square-planar surface at the binding site, such that the metal–CO₂ interaction closely represents a surface normal. The CO₂ rotations denoted by the red arrows are rotations about the surface normal (largely parallel to the metal–oxygen plane), while those denoted by blue arrows are rotations away from that surface normal. For Mg-MOF-74, the mode energies corresponding to the motions denoted by the red and blue arrows are 4.3 and 8.5 meV, respectively. For HKUST-1, the mode energies corresponding to the motions denoted by the red and blue arrows are 0.2 and 3.4 meV, respectively. Color scheme of the framework atoms: Mg, light blue; Cu, blue; C, gray; O, red; and H, white. Color scheme of the CO₂ atoms: C, gray; O, purple. (c) Potential energy curves of the two rotational motions of adsorbed CO₂ on an open Cu site in HKUST-1, derived from DFT-LDA calculations. Red and blue data points correspond to the CO₂ rotations denoted by the red and blue arrows in (b), respectively.

degree of O–C–O bond bending derived from the diffraction data refinement to be much larger than what our calculation suggests. We emphasize that the bond angle derived from the diffraction data is a structural average and can be strongly biased by the relatively large disorder of the adsorbed CO₂ and thus does not reflect the real bond angle accurately. Since CO₂ is reversibly physisorbed on these open metal sites, a large degree of CO₂ bond activation and bending is indeed very unlikely. This is further supported by frozen phonon

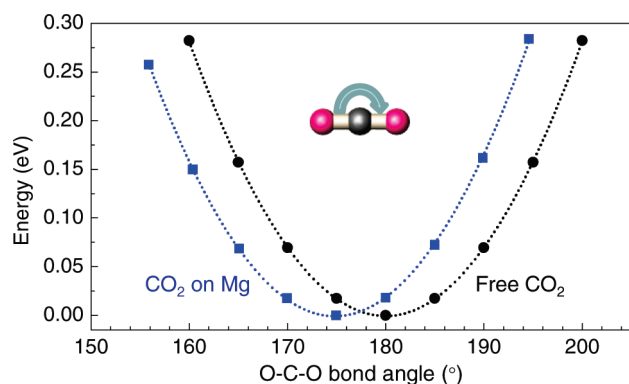


Figure 4. Potential energy curves of the O–C–O bending motion for a free CO₂ molecule and the CO₂ adsorbed on open Mg in Mg-MOF-74, derived from DFT-LDA calculations.

calculations of the O–C–O bond bending mode. In Figure 4, the potential energy was plotted as a function of the O–C–O bond angle for both a free CO₂ molecule and the CO₂ adsorbed on open Mg. For bond bending to account for the $\sim 20^\circ$ bond angle distortion derived from diffraction data, there would be a significant energy penalty of ~ 150 meV/CO₂.

Our clarifications on the nature of CO₂ binding on the open metal centers in MOFs have important implications for CO₂ storage and separation applications. The open metals possess strong enough affinity toward CO₂ such that it is capable of storing CO₂ at ambient conditions or preferentially adsorbing CO₂ over other gases (such as CH₄) during a dynamic separation.⁸ At the same time, the interaction is not too strong such that the CO₂ molecules can be conveniently released from the MOF material when needed. Indeed, CO₂ adsorption in Mg-MOF-74 is fully reversible even at room temperature,⁷ while heating at 80 °C was found to be useful to efficiently remove CO₂ from Mg-MOF-74 in column breakthrough measurements.⁸ This excellent balance between adsorption and regeneration capabilities makes open metal sites one of the most important structural features to consider when developing MOFs for CO₂ capture applications.

In summary, we have clearly identified the major CO₂ adsorption sites in Mg-MOF-74 and HKUST-1 through neutron diffraction measurements. In both MOFs, the open metal ions provide the strongest binding sites through enhanced electrostatic interaction between the open metal charge and the CO₂ multipole moments. Vibrational mode analysis of the adsorbed CO₂ based on first-principles calculations shows that the adsorbed CO₂ molecule is attached to the metal sites in an end-on orientation with the closest oxygen fixed while the rest of the molecule is quite “loose” (i.e., orientationally free). This high orientational disorder leads to the appearance of significantly larger bond bending in diffraction analysis as compared to that in DFT calculations. Both LDA and GGA calculations clearly show that the deviation of the O–C–O bond from linear is modest and suggest that the nature of the CO₂–metal interaction is still physisorptive and desorption should not be difficult. These results provide useful information for further development of new MOF materials toward CO₂-adsorption-related applications.

SUPPORTING INFORMATION AVAILABLE Neutron diffraction data of bare Mg-MOF-74 and HKUST-1 and crystallographic details of the CO₂ adsorption sites derived from the diffraction data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ACKNOWLEDGMENT This work was partially supported by the U.S. Department of Energy through BES Grant No. DE-FG02-08ER46522 (T.Y.). J.M.S. acknowledges support from the National Research Council Postdoctoral Associate Program.

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