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# CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub> adsorption in Zn<sup>2+</sup>-containing zeolites and metal–organic frameworks

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We employ a chemically accurate ( $\pm 4$  kJ mol<sup>-1</sup>) embedding approach to calculate enthalpies for CO<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub> adsorption in the Zn<sup>2+</sup>-containing zeolites FAU and CHA, and for CO<sub>2</sub> and H<sub>2</sub> in the metal–organic frameworks (MOFs) Zn-MOF-74 and CALF-20. Using MP2 as the high-level method and PBE+D4 as the periodic low-level method (MP2:PBE+D4), we obtain CO<sub>2</sub> adsorption enthalpies of  $-46$ ,  $-34$ , and  $-36$  kJ mol<sup>-1</sup> for Zn-CHA, Zn-MOF-74, and CALF-20, respectively, all within chemical accuracy limits of the experimental values of  $-42$ ,  $-30$ , and  $-39$  kJ mol<sup>-1</sup>. For CO<sub>2</sub> in Zn-FAU, where no experimental data exist, we provide an MP2:PBE+D4 prediction of  $-49$  kJ mol<sup>-1</sup>. For N<sub>2</sub>, we predict MP2:PBE+D4 adsorption enthalpies of  $-41$  and  $-39$  kJ mol<sup>-1</sup> in Zn-CHA and Zn-FAU, respectively. CO<sub>2</sub> adsorption is stronger in the zeolites than in the studied MOFs. Across all systems, CO<sub>2</sub> adsorption tends to be stronger than N<sub>2</sub> adsorption and both are largely favoured over H<sub>2</sub>. We observe inconsistent accuracy of PBE+D4 for the two MOFs, despite their similar characteristics, underscoring the need for high-level approaches in predictive screening. Additionally, we conclude that Zn<sup>2+</sup> cations with open coordination sites act as the primary binding sites and that these cations preferentially occupy 6-membered rings in zeolites.

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## 1. Introduction

As the world transitions from fossil fuels to cleaner sources of energy, hydrogen is emerging as a promising candidate.<sup>1</sup> At present, it is mainly produced through steam reforming,<sup>2</sup> a process that involves separating CO<sub>2</sub> from H<sub>2</sub>. The CO<sub>2</sub> adsorption characteristics are also important for carbon capture techniques such as pressure swing adsorption (PSA)<sup>3</sup> and direct air capture (DAC).<sup>4–6</sup> These applications typically rely on gas adsorption into porous solid sorbents with high adsorption capacity, selectivity, reusability, and stability.<sup>7–10</sup> Zeolites are a class of materials that has been extensively used over the last decades for gas storage and as molecular sieves, in addition to their importance in heterogeneous catalysis.<sup>11–15</sup> However, recent advances in CO<sub>2</sub> capture have focused on metal–organic frameworks (MOFs) due to their chemical versatility.<sup>16–22</sup>

Zeolites, such as faujasite (FAU) and chabazite (CHA) with low Si/Al ratios, *i.e.*, high Al concentrations, are viable materials for effective CO<sub>2</sub> capture.<sup>23–27</sup> Incorporating metal cations,

which balance the negative charges introduced by aluminium substitution into the framework, is a promising route to enhance (selective) adsorption. Among these zeolites, Zn-exchanged CHA with high Si/Al ratios has shown CO<sub>2</sub> adsorption capacities comparable to zeolite 13X of the FAU type.<sup>28</sup> Additionally, Mg<sup>2+</sup>, Ca<sup>2+</sup>, and Zn<sup>2+</sup> have been identified as the most effective cations for selective CO<sub>2</sub> adsorption in gas mixtures among a set of investigated extra-framework metal cations.<sup>29</sup> Further, the Zn<sup>2+</sup>-containing MOF CALF-20 displayed CO<sub>2</sub> selectivity over N<sub>2</sub> and even over water,<sup>30</sup> both of which can be ubiquitous under practical operating conditions. For reversible physisorption, the ideal heat of adsorption lies between  $-30$  and  $-60$  kJ mol<sup>-1</sup>.<sup>16–20</sup> However, despite extensive experimental and computational studies, reported adsorption enthalpies vary widely, leading to uncertainty in the understanding of the underlying mechanisms and the reliability of predictions for adsorption processes.<sup>31–34</sup>

Yet, in the quest for accelerating materials development for (selective) CO<sub>2</sub> adsorption, understanding and accurately predicting adsorption strength and selectivity remains a key challenge. The adsorption properties are primarily influenced by the structure of the porous framework and by the distribution, position, and type of defects, framework-substituted sites, and extra-framework species within the materials.<sup>35–37</sup> To assess the accuracy of simulations, it is crucial to validate commonly used, approximate methods such as density functional theory (DFT),

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through comparison to chemically accurate ( $\pm 4$  kJ mol<sup>-1</sup>), yet more computationally demanding, methods like second-order Møller-Plesset perturbation theory (MP2),<sup>38</sup> or to experiments.

In this work, we achieve chemical accuracy for CO<sub>2</sub> and H<sub>2</sub> adsorption at Zn<sup>2+</sup> sites in the medium-pore zeolite CHA, and the Zn<sup>2+</sup>-containing MOFs MOF-74 and CALF-20. Additionally, we provide predictions for the CO<sub>2</sub> adsorption enthalpies in Zn-FAU and for N<sub>2</sub> adsorption in Zn-CHA and Zn-FAU, for which no experimental data are available. To go beyond standard DFT, we employ a hybrid high-level quantum mechanics (QM): low-level QM subtractive mechanical embedding approach.<sup>39–43</sup> This method combines DFT with periodic boundary conditions (pbc) using the Perdew–Burke–Ernzerhof (PBE)<sup>44,45</sup> functional, augmented with Grimme's D4 dispersion correction,<sup>46,47</sup> and MP2 as the high-level method (denoted MP2:PBE+D4). As we will show in this work, at this level, the calculated CO<sub>2</sub> adsorption enthalpies for Zn-CHA, CALF-20, and Zn-MOF-74 deviate from experimental values by only 4, 3, and 4 kJ mol<sup>-1</sup>, respectively,<sup>28,30,48</sup> and the binding of CO<sub>2</sub> tends to be preferred over N<sub>2</sub>, and both bind significantly stronger than H<sub>2</sub>.

## 2. Systems and models

### 2.1. Zeolites and metal–organic frameworks

The systems investigated in this study include FAU, CHA, MOF-74, and CALF-20, chosen for their relevance to gas adsorption.<sup>24,25,49–51</sup> Zn<sup>2+</sup> is selected as the extra-framework cation due to its ionic radius being similar to that of divalent alkaline earth metals such as Ca<sup>2+</sup> and Mg<sup>2+</sup>, as well as to that of Li<sup>+</sup>, all of which are highly effective for CO<sub>2</sub> adsorption.<sup>28,52</sup> Moreover, Zn<sup>2+</sup> offers higher coordinative flexibility<sup>53</sup> and binds more strongly with CO<sub>2</sub> due to higher Lewis acidity compared to Ca<sup>2+</sup> and Mg<sup>2+</sup> cations.<sup>53,54</sup> Furthermore, Zn<sup>2+</sup> is more abundant and more affordable compared to Li<sup>+</sup>, which is among the most used and best-performing cations for CO<sub>2</sub> adsorption,<sup>24</sup> rendering Zn<sup>2+</sup> a promising candidate to enhance (selective) CO<sub>2</sub> capture. Additionally, Zn<sup>2+</sup> sites, as found in different MOFs and enzymes, are also known to interact strongly with CO<sub>2</sub> molecules.<sup>55,56</sup>

The coordination environment of Zn<sup>2+</sup> cations can vary across the investigated zeolites CHA and FAU, and even within the same framework, depending on the specific cation location. In CHA, the coordination of Zn<sup>2+</sup> changes from a rather symmetric threefold coordination by framework oxygen atoms in six-membered rings (6MR) to a less symmetric threefold coordination in eight-membered rings (8MR), see Fig. 1(a). In FAU, Zn<sup>2+</sup> similarly exhibits a symmetric, threefold coordination in 6MRs at sites I and II and a symmetric, but fourfold coordination at site III, see Fig. 1(b).

For MOF-74 and CALF-20, in contrast to the zeolites, Zn<sup>2+</sup> cations are incorporated into the framework and are fivefold coordinated. In MOF-74, the Zn<sup>2+</sup> coordination is square pyramidal (see Fig. 2), whereas in CALF-20, it is trigonal bipyramidal, as shown in Fig. 3. In the investigated MOFs, only one type of Zn<sup>2+</sup> site exists in each framework, at variance with the investigated zeolites, which contain different adsorption sites.

### 2.2. Models

The supercells used for the large-pore zeolite FAU are based on the unit cell taken from the International Zeolite Association (IZA) database.<sup>57</sup> To compensate for the charge of the introduced extra framework metal cations, Li<sup>+</sup> or Zn<sup>2+</sup>, one or two Al atoms are incorporated into the zeolite framework, which leads to Si/Al ratios of 23 or 47, respectively. The simulation cells of the medium-pore zeolite CHA are obtained by multiplying the cell taken from the IZA database.<sup>57</sup> The simulation cell contains two aluminium atoms, resulting in a Si/Al ratio of 17. Al atoms are distributed according to Löwenstein's rule.<sup>58</sup> The optimised cell parameters for both FAU and CHA are given in Table S1 in the Supplementary Information (SI). Our nomenclature adheres to the recommendations of the IZA database<sup>57</sup> and is explained in Section S1 in the SI. Our models are not aimed at representing the exact experimental Si/Al ratios. Rather, we create models that mimic the local environments likely present in the experimental Si/Al regimes. Models of Zn-MOF-74 and CALF-20 are derived from the Cambridge Crystal Database (CSD).<sup>59</sup> Our Zn-MOF-74 model is based on a Niggli-reduced rhombohedral unit cell containing six Zn<sup>2+</sup> ions connected by three (dobdc)<sup>4-</sup> organic linkers, resulting in 54 atoms per simulation cell. The CALF-20 simulation cell consists of 44 atoms with four Zn<sup>2+</sup> centers. For all systems, only one molecule of CO<sub>2</sub>, N<sub>2</sub>, or H<sub>2</sub> is considered per simulation cell to focus on the adsorbate–substrate interactions in the low-coverage regime.

## 3. Methods

We extend beyond the standard computational approach, which relies on DFT with pbc and dispersion (DFT-D), by adopting a QM:QM approach. We use DFT-D as the low-level method to compute the potential energy surface (PES) for the entire periodic structure, while employing MP2 as the high-level method for cluster models to locally describe the interactions between the adsorbed molecule and the nearby framework. Hybrid MP2:DFT-D provides chemical accuracy for alkane adsorption in zeolites,<sup>38,60–64</sup> while a small but noticeable additional correction from MP2 to CCSD(T) has been observed for systems with strong hydrogen bonds.<sup>62,63</sup> The MP2:DFT-D approach is used for single point calculations for the most stable DFT-optimised adsorption structures only.

### 3.1. Adsorption energies and enthalpies

We use DFT-D to obtain the enthalpy of adsorption ( $H_{\text{ad}}$ ), which is given by

$$H_{\text{ad}} = E_{\text{ad}} + E_{\text{ZPV}} + E_{\text{therm}} - RT, \quad (1)$$

where  $E_{\text{ad}}$  corresponds to electronic adsorption energies,  $E_{\text{ZPV}}$  refers to contributions of zero-point vibrational energies,  $E_{\text{therm}}$  to thermal energy corrections, and  $R$  to the universal gas constant. The adsorption energy ( $E_{\text{ad}}$ ) is defined as the difference between the energy of the framework loaded with the gas molecule (referred to as the adsorbed complex,  $E_{\text{AS}}$ ), and the



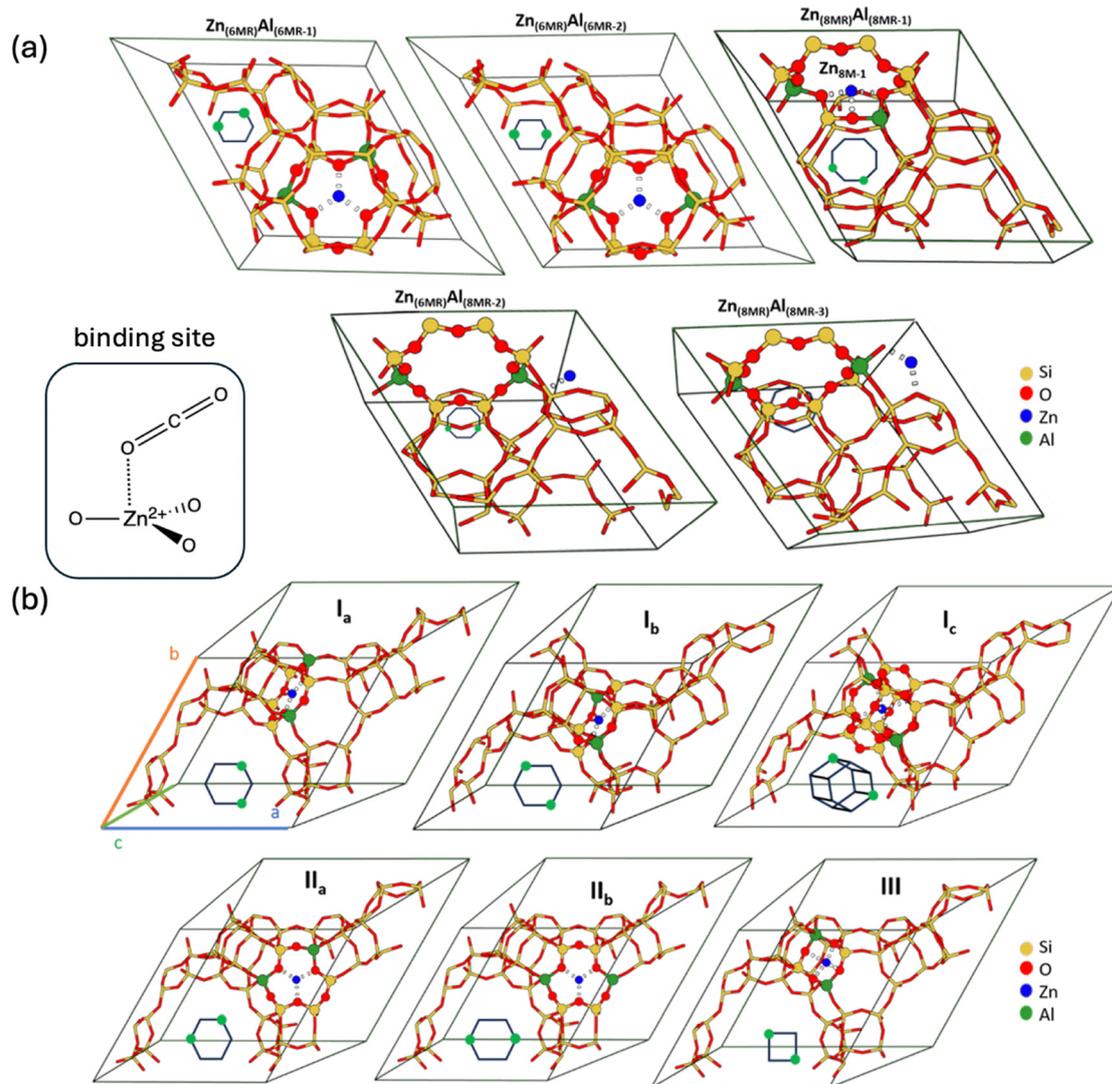


Fig. 1 Types of sites available in (a) CHA and (b) FAU for the location of extra framework cations, along with different Al distributions shown in 6MRs, 8MRs, and, in the case of FAU, for 4MRs. Dotted lines indicate attractive interactions between  $\text{Zn}^{2+}$  cations and adjacent framework oxygen atoms. The coordination environment of a  $\text{Zn}^{2+}$  cation binding to  $\text{CO}_2$  is shown as well.

sum of energies of the gas molecule surrounded by vacuum ( $E_A$ ) and the unloaded framework ( $E_S$ ) within their relaxed structures,

$$E_{\text{ad}} = E_{\text{AS}} - (E_A + E_S). \quad (2)$$

### 3.2. Hybrid QM:QM calculations

For MP2:DFT-D calculations, the hybrid MP2:DFT-D electronic energy is defined as

$$E_{\text{MP2}}(\text{S}) \approx E_{\text{MP2:DFT-D}}(\text{S}, \text{C}) = E_{\text{DFT-D}}(\text{S}) + \Delta E_{\text{HL}}(\text{C}), \quad (3)$$

where  $\Delta E_{\text{HL}}(\text{C})$  is the high-level correction given by

$$\Delta E_{\text{HL}}(\text{C}) = E_{\text{MP2}}(\text{C}) - E_{\text{DFT-D}}(\text{C}). \quad (4)$$

$E_{\text{MP2}}(\text{C})$  denotes the MP2 energy of a cluster model C, describing the adsorption site.  $E_{\text{DFT-D}}(\text{C})$  and  $E_{\text{DFT-D}}(\text{S})$  refer to the

DFT-D energies of the same cluster model and the full periodic system, respectively. The MP2 quality adsorption enthalpy is then calculated as

$$H_{\text{ad}}(\text{MP2}) = E_{\text{ad,MP2:DFT-D}} + (E_{\text{ZPV}} + E_{\text{therm}})_{\text{DFT-D}} - RT. \quad (5)$$

The MP2:DFT-D adsorption energies are combined with the zero-point vibrational energy and thermal contributions calculated with DFT with pbc. Lastly, the Gibbs free energy of adsorption ( $G_{\text{ad}}$ ) is calculated using:

$$G_{\text{ad}} = H_{\text{ad}} - T\Delta S_{\text{ad}}, \quad (6)$$

where  $T$  is the temperature, and  $\Delta S_{\text{ad}}$  is the adsorption entropy.

### 3.3. Computational details

**3.3.1. Density functional theory.** DFT calculations employing the PBE functional,<sup>44,45</sup> augmented with Grimme's  $\text{D2}^{46}$



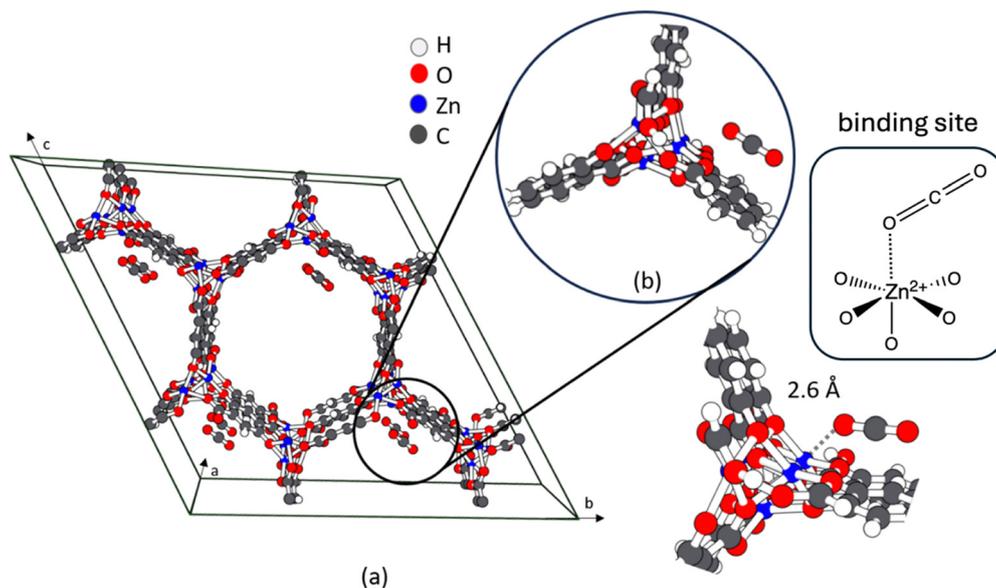


Fig. 2 (a) Periodic Zn-MOF-74 model, (b) cluster model for CO<sub>2</sub> adsorption. Cluster models are cut out of the periodic optimized structure of Zn-MOF-74 and used for MP2:PBE+D4 single point calculations. The dotted line indicates the shortest distance between a Zn<sup>2+</sup> cation and an oxygen atom of the CO<sub>2</sub> molecule. The coordination environment of a Zn<sup>2+</sup> cation binding to CO<sub>2</sub> is shown as well.

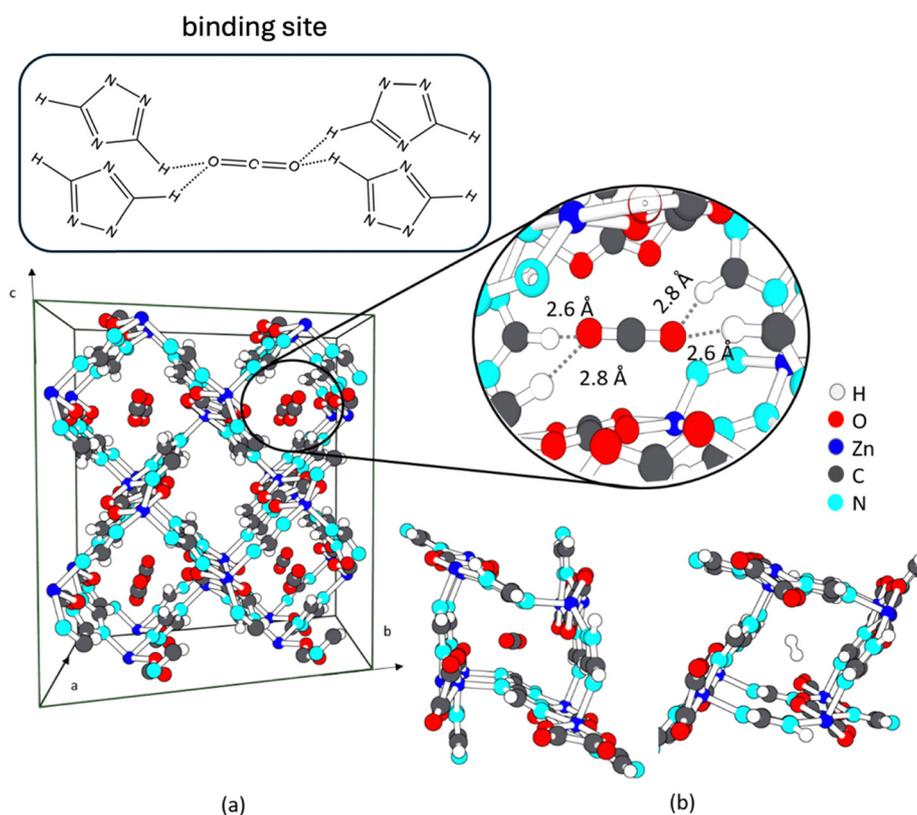


Fig. 3 (a) Periodic CALF-20 model, (b) cluster model for CO<sub>2</sub>/H<sub>2</sub> adsorption. Cluster models are cut out of the periodic optimized structure of CALF-20 and used for MP2:PBE+D4 single point calculations. The dotted lines indicate the distances between framework hydrogen atoms and the oxygen atoms of the CO<sub>2</sub> molecule. The coordination environment of a Zn<sup>2+</sup> cation binding to CO<sub>2</sub> is shown as well.

and D4<sup>47</sup> dispersion corrections, are conducted using the Vienna *ab initio* package (VASP)<sup>65,66</sup> version 5.4.1 and 6.2.1,

respectively. These calculations make use of a plane-wave basis set for valence electrons, and the projector augmented wave



(PAW)<sup>67</sup> method for core electrons. Structure optimisations are performed with energy cutoffs of 400 eV (for FAU, CHA, and CALF-20) and 900 eV for MOF-74. Cell shape and size optimisations are performed using an energy cutoff of 800 eV to reduce the volume change effects on basis sets and are iterated until convergence is reached for all above-mentioned frameworks except MOF-74, for which 900 eV is used. The Brillouin zone is sampled at the  $\Gamma$ -point only. Convergence thresholds are set to  $10^{-7}$  eV for electronic energy changes and  $0.005 \text{ eV } \text{\AA}^{-1}$  for structure optimisations. Stationary points are confirmed through a normal mode analysis by ensuring that no imaginary frequencies are observed. PBE+D2 and PBE+D4 numerical Hessians are computed using central finite differences with Cartesian displacements of 1 pm and an energy convergence threshold of  $10^{-8}$  eV to determine harmonic zero-point vibrational energies and thermal enthalpy contributions, as well as entropies using the MonaLisa code.<sup>40,68</sup> The results obtained with PBE+D4 are reported in the main text, and for PBE+D2 in the SI.

**3.3.2. Post-Hartree-Fock methods.** Hybrid QM:QM calculations<sup>39,41-43,69</sup> employ a subtractive mechanical embedding scheme to achieve an MP2<sup>70</sup> quality PES using the MonaLisa code.<sup>40,68</sup> A cluster comprising the adsorbate and part of the framework in its vicinity is extracted from the periodic structure, ensuring a conservative distance of at least 10  $\text{\AA}$  around the  $\text{CO}_2$ ,  $\text{N}_2$ , or  $\text{H}_2$  molecules. For the cluster models of FAU, CHA, MOF-74, and CALF-20, the dangling bonds are saturated with H atoms as explained in Section S1 in the SI. The structures of the clusters are illustrated in Fig. 2 and 3, as well as S1 and S2 in the SI. Single point cluster calculations are corrected for the basis set superposition error (BSSE)<sup>71</sup> using the Counterpoise correction and carried out with the ORCA program,<sup>72-74</sup> version 5.03, employing the def2-TZVP<sup>75-77</sup> basis sets for PBE+D4 cluster calculations. Additionally, domain-based local pair natural orbital (DLPNO) MP2<sup>78,79</sup> energies are extrapolated to the complete basis set limit using a two-point extrapolation scheme<sup>80,81</sup> with cc-pVXZ basis sets ( $X = \text{T}, \text{Q}$ ).<sup>82,83</sup> The ‘TightPNO’ and ‘TightSCF’ settings are applied. The term ‘DLPNO’ is omitted hereafter for brevity. Example inputs are provided as part of the SI.

## 4. Results and discussions

### 4.1. Extra-framework cation location in the zeolites FAU and CHA

For FAU and CHA, we first examine the influence of the Al atom distribution in the zeolite frameworks on the preferred extra-framework cation locations. Different distributions of pairs of Al atoms in the framework are investigated for  $\text{Zn}^{2+}$  binding, as illustrated in Fig. 1(a) for CHA and in Fig. 1(b) for FAU. Tables S2 and S3 in the SI present the relative energies of  $\text{Zn}^{2+}$  and  $\text{Li}^+$  binding to different sites in FAU.

For  $\text{Zn}^{2+}$ -containing CHA, X-ray diffraction (XRD), infrared (IR), and ultraviolet-visible (UV-vis) experiments<sup>28</sup> indicate that, depending on the synthesis, there are three distinct cation

types:  $\text{Zn}^{2+}$ ,  $\text{Zn}(\text{OH})^+$ , and  $\text{H}^+$ . The trends for  $\text{Zn}^{2+}$ -containing CHA are presented in Table S4, while Tables S7 and S8 in the SI show the relative binding energies for  $\text{Zn}(\text{OH})^+$  and  $\text{H}^+$ .

For FAU, the trends for both cations ( $\text{Li}^+$  and  $\text{Zn}^{2+}$ ) are similar, with location at site II exhibiting the highest stability, followed by site I, and then site III. Cation adsorption at site III is least stable due to the strain induced by entering the small four-membered ring, in contrast to the more spacious six-membered rings of sites I and II. The higher stability of the  $\text{Zn}^{2+}$  cation at site II compared to site I may be attributed to its environment. Site II is located within a 6MR and opens into the larger 12MR. In contrast, site I, which is also situated in a 6MR, is confined within the sodalite cage of the FAU framework.

For CHA,  $\text{Zn}^{2+}$  cation adsorption in 6MRs is more stable than in 8MRs with a difference of more than  $70 \text{ kJ mol}^{-1}$  because, in 6MRs, the  $\text{Zn}^{2+}$  cation is symmetrically coordinated to three O atoms of the framework, exhibiting very similar bond distances from 1.95 to 1.98  $\text{\AA}$ , whereas, within 8MRs,  $\text{Zn}^{2+}$  is only directly bonded to one O atom with a distance of 1.97  $\text{\AA}$ . Even when two Al atoms are located in an 8MR,  $\text{Zn}^{2+}$  preferentially binds to a nearby 6MR. We denote such configurations as  $\text{Zn}_{(6\text{MR})}\text{Al}_{(8\text{MR}-2)}$ , where the subscript on Zn indicates the ring in which the  $\text{Zn}^{2+}$  cation is located (here, a 6MR), and the subscript on Al denotes the ring containing the two Al atoms (here, an 8MR). The following number refers to the number of Si-containing T-sites separating the two Al atoms (in this case, 2). The binding energy for  $\text{Zn}^{2+}$  in this case is very similar to the case where  $\text{Zn}^{2+}$  is located in a 6MR with the two Al atoms located in the same 6MR,  $\text{Zn}_{(6\text{MR})}\text{Al}_{(6\text{MR}-2)}$ . This suggests that for  $\text{Zn}^{2+}$  ions, the direct coordination environment, specifically the binding to framework oxygen atoms, plays a more important role than the proximity to framework Al atoms, which induce the negative charge in the framework. In contrast, for the protonated species, the proton is most stable when attached to an oxygen atom that is directly connected to an Al atom.

The relative energies for different locations of  $\text{Zn}(\text{OH})^+$  and protons in CHA are shown in Tables S7 and S8 in the SI, respectively. When  $\text{Zn}(\text{OH})^+$  is placed into a 6MRs, it is not stable and becomes protonated by the second Brønsted acid site (BAS), forming  $\text{Zn}(\text{OH}_2)^{2+}$ . Therefore, the formation of  $\text{Zn}(\text{OH})^+$  is only expected in high Si/Al samples without nearby excess protons that can form water coordinated to  $\text{Zn}^{2+}$ , or, if Al pairs are present in 8MRs of the CHA framework. This deviates from the preferred binding site of  $\text{Zn}^{2+}$  in 6MRs. Additionally,  $\text{Zn}(\text{OH})^+$  binding within 8MRs exhibits the highest stability in the configuration where two Al atoms are separated by two Si units in the same 8MR, ( $\text{Zn}(\text{OH})_{(8\text{MR})}^+\text{Al}_{(8\text{MR}-2)}$ ). This configuration is more stable by 9 and  $30 \text{ kJ mol}^{-1}$  compared to  $\text{Zn}(\text{OH})^+$  in 8MR with two Al atoms separated by three Si units ( $\text{Zn}(\text{OH})_{(8\text{MR})}^+\text{Al}_{(8\text{M}-3)}$ ) or one Si unit ( $\text{Zn}(\text{OH})_{(8\text{MR})}^+\text{Al}_{(8\text{M}-1)}$ ), respectively.

For  $\text{Zn}^{2+}$ -containing CHA, our energy-based assignment of cation binding locations to framework oxygen atoms is corroborated by our calculated IR stretching frequencies, particularly around 850 and  $916 \text{ cm}^{-1}$  (reported in Table S4 in the SI). These frequencies, varying by  $66 \text{ cm}^{-1}$ , correspond to perturbed



T–O–T framework vibrations near the cations located within the 6MRs and 8MRs of CHA, respectively. The results might be considered consistent with experiments,<sup>28</sup> reporting IR stretching frequencies for T–O–T vibrations of 902 and 950  $\text{cm}^{-1}$  for the 6MRs and 8MRs in CHA, respectively,<sup>28</sup> which differ by 48  $\text{cm}^{-1}$ . Further, the bands are experimentally found to form in two stages,<sup>28</sup> which is consistent with our findings, suggesting that the 6MRs become populated by divalent  $\text{Zn}^{2+}$  cations before the 8MRs do so.

For extra-framework  $\text{Zn}(\text{OH})^+$  species, the calculated scaled harmonic IR frequency of the O–H stretching of  $\text{Zn}(\text{OH})^+$  located in 8MRs ranges from 3644 to 3675  $\text{cm}^{-1}$  for different Al pair distributions, as shown in Table S7 in the SI. Following the literature,<sup>84,85</sup> the scaling approach is explained in Section S2 of the SI. When compared to the experimentally reported O–H stretching frequency for  $\text{Zn}(\text{OH})^+$  in CHA, 3665  $\text{cm}^{-1}$ ,<sup>28</sup> our results are consistent with  $\text{Zn}(\text{OH})^+$  being located in 8MR and best agree for  $\text{Zn}(\text{OH})_{(8\text{MR})}^+ \text{Al}_{(8\text{MR}-2)}$ , which we also predict to be the most stable adsorption site for  $\text{Zn}(\text{OH})^+$ , see Table S7 in the SI.

## 4.2. $\text{CO}_2$ , $\text{N}_2$ , and $\text{H}_2$ adsorption

**4.2.1. FAU and CHA zeolites.** After having identified the most stable and thus most likely adsorption sites for the extra-framework species in the two zeolites FAU and CHA, we investigate the adsorption of  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{H}_2$  at these  $\text{Zn}^{2+}$  sites. Table 1 presents the adsorption energies and enthalpies for  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{H}_2$  adsorption on sites I, II, and III in Zn-FAU, calculated using PBE+D4. In Zn-FAU, site III exhibits the most exothermic adsorption of  $\text{CO}_2$  and  $\text{H}_2$ , followed by sites I and II. However, as explained before, site III is the least stable  $\text{Zn}^{2+}$  location. Thus, the strong adsorption of  $-82 \text{ kJ mol}^{-1}$  can be attributed to the low stability and thus higher reactivity of the  $\text{Zn}^{2+}$  in this location. While adsorption at site III is predicted to be strongest, the presence of this site in real samples is unlikely due to its instability, and therefore, it is not expected to contribute significantly to experimental observations. In contrast, site II, which is the preferred  $\text{Zn}^{2+}$  location, exhibits the weakest  $\text{CO}_2$  adsorption of  $-48 \text{ kJ mol}^{-1}$ , yet is expected to be most relevant in experimental samples.

**Table 1** Calculated relative  $\text{Zn}^{2+}$  binding energies ( $E_{\text{site}}$ ), adsorption energies ( $E_{\text{ad}}$ ), and enthalpies ( $H_{\text{ad}}$ ) at 298 K for  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{H}_2$  adsorption in Zn-FAU (Si/Al = 23), obtained using PBE+D4. Also reported are zero-point energy corrections ( $\Delta E_{\text{ZPE}}$ ), thermal contributions ( $\Delta E_{\text{therm}}$ ), entropy contributions ( $-\text{T}\Delta S_{\text{ad}}$ ), and relative Gibbs free energies ( $G_{\text{ad}}$ ), all in  $\text{kJ mol}^{-1}$ , at a pressure of 0.1 MPa

Adsorbate	Site	$E_{\text{site}}$	$E_{\text{ad}}$	$\Delta E_{\text{therm}}$	$\Delta E_{\text{ZPE}}$	$H_{\text{ad}}$	$-\text{T}\Delta S_{\text{ad}}$	$G_{\text{ad}}$
$\text{CO}_2$	I <sub>a</sub>	9	-64	1	5	-58	37	-21
	II <sub>a</sub>	0	-48	-2	6	-44	43	-2
	III	128	-82	1	5	-76	49	-27
$\text{N}_2$	II <sub>a</sub>	0	-38	-4	3	-39	43	4
$\text{H}_2$	I <sub>a</sub>	9	-20	-4	7	-17	24	7
	II <sub>a</sub>	0	-22	-4	8	-18	26	8
	III	128	-45	-5	9	-41	26	-15

In general, in agreement with literature,<sup>29</sup> the adsorption of  $\text{CO}_2$  is stronger than that of  $\text{N}_2$ , and both are significantly stronger than  $\text{H}_2$  adsorption, indicating that Zn-FAU preferentially adsorbs  $\text{CO}_2$ , then  $\text{N}_2$ , and only very weakly  $\text{H}_2$ . On site II, the adsorption enthalpy of  $\text{CO}_2$  is  $-44 \text{ kJ mol}^{-1}$ .  $\text{N}_2$  adsorption is 5  $\text{kJ mol}^{-1}$  less exothermic,  $-39 \text{ kJ mol}^{-1}$ , and, for  $\text{H}_2$ , it is only  $-18 \text{ kJ mol}^{-1}$ . Additionally, variations of as much as 20 to 40  $\text{kJ mol}^{-1}$  occur for  $\text{CO}_2$  and  $\text{H}_2$  adsorption across different  $\text{Zn}^{2+}$  locations. The Gibbs free energies of  $\text{CO}_2$  adsorption in Zn-FAU at all sites are negative, even though they reach  $-2 \text{ kJ mol}^{-1}$  for site II, which is nearly thermoneutral.  $\text{N}_2$  adsorption at site II is slightly endergonic, with a Gibbs free energy of adsorption of 4  $\text{kJ mol}^{-1}$ . While  $\text{CO}_2$  adsorption is exergonic across the framework, for  $\text{H}_2$ , only site III would allow spontaneous adsorption applying standard temperature and pressure. For comparison, adsorption energies and enthalpies calculated for  $\text{CO}_2$  and  $\text{H}_2$  on  $\text{Zn}^{2+}$  and  $\text{Li}^+$  using PBE+D2 are reported in Tables S5 and S6 in the SI, and discrepancies of 2 to 10  $\text{kJ mol}^{-1}$  are observed. Comparing both cations indicates that the adsorption trends are similar for sites I and II, but not for site III. At site III, adsorption energies obtained for  $\text{Li}^+$  are weaker than for  $\text{Zn}^{2+}$ , which is attributed to the higher stability of the  $\text{Li}^+$  cation at site III. This might be because in Li-FAU, only one Si is replaced by one Al, so site III is less strained in comparison to Zn-FAU, where two Al atoms replace two Si atoms.

We note that for weakly bound adsorbates, most notably  $\text{H}_2$  in our study, our approach to computing adsorption enthalpies, entropies, and Gibbs free energies using a harmonic treatment around a single optimised configuration has inherent limitations. While a single optimised minimum provides a well-defined reference structure, weak adsorption corresponds to a shallow potential energy surface. Under such conditions, finite-temperature effects and anharmonicity may cause the adsorbate to sample multiple configurations or to diffuse into the pore rather than remain localized at a single binding site. For such cases, approaches based on molecular dynamics or Monte Carlo sampling would provide a more rigorous description of adsorption thermodynamics. In principle, adsorption enthalpies and free energies could be obtained from such simulations, ideally based on an MP2-quality potential energy surface. However, combining high-level electronic structure methods with extensive sampling would be computationally very demanding and is beyond the scope of the present work.

A proper finite-temperature description of weakly interacting alkanes in acidic zeolites has been achieved previously by some of us,<sup>61</sup> demonstrating that adsorption strengths are indeed reduced by a few  $\text{kJ mol}^{-1}$  when these effects are accounted for. Accordingly, the thermodynamic quantities reported here, which are based on the most stable binding motif, should be viewed as upper limits to the adsorption strength. Importantly, however, our calculated enthalpies for the more strongly binding  $\text{CO}_2$  are in good agreement with experimental heats of adsorption, indicating that finite-temperature and anharmonic effects do not play a major role for  $\text{CO}_2$ . Moreover, these effects are expected to be least pronounced for the strongest adsorbate,  $\text{CO}_2$ , and most



**Table 2** Calculated  $\text{Zn}^{2+}$  binding energies ( $E_{\text{site}}$ ), adsorption energies ( $E_{\text{ad}}$ ), and enthalpies ( $H_{\text{ad}}$ ) at 298 K for  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{H}_2$  adsorption in Zn-CHA ( $\text{Si}/\text{Al} = 17$ ), obtained using PBE+D4. Also reported are zero-point energy corrections ( $\Delta E_{\text{ZPV}}$ ), thermal contributions ( $\Delta E_{\text{therm}}$ ), entropy contributions ( $-T\Delta S_{\text{ad}}$ ), and relative Gibbs free energies ( $G_{\text{ad}}$ ), all in  $\text{kJ mol}^{-1}$ , at a pressure of 0.1 MPa. Scaled PBE+D4 wavenumbers of  $\text{CO}_2$  asymmetric stretching vibrations ( $\nu_{\text{CO}_2}$ ) and non-scaled stretching frequencies of T–O–T vibrations are given in  $\text{cm}^{-1}$

Adsorbate	Site	$E_{\text{site}}$	$E_{\text{ad}}$	$\Delta E_{\text{therm}}$	$\Delta E_{\text{ZPV}}$	$H_{\text{ad}}$	$-T\Delta S_{\text{ad}}$	$G_{\text{ad}}$	$\nu_{\text{T-O-T}}$	$\nu_{\text{CO}_2}$
$\text{CO}_2$	$\text{Zn}_{(6\text{MR})}\text{Al}_{(6\text{MR}-1)}$	10	−56	−1	6	−51	41	−10	837	2352 <sup>a</sup>
	$\text{Zn}_{(6\text{MR})}\text{Al}_{(6\text{MR}-2)}$	0	−56	−1	6	−51	42	−9	850	2357 <sup>a</sup>
	$\text{Zn}_{(8\text{MR})}\text{Al}_{(8\text{MR}-1)}$	84	−20	−4	10	−14	58	44	902 <sup>b</sup>	2356 <sup>b</sup>
	$\text{Zn}_{(6\text{MR})}\text{Al}_{(8\text{MR}-2)}$	1	−56	−1	6	−50	43	−7	916	2348 <sup>a</sup>
									950 <sup>b</sup>	2351 <sup>a</sup>
	$\text{Zn}_{(8\text{MR})}\text{Al}_{(8\text{MR}-3)}$	76	−63	−1	6	−58	42	−16	900	2353 <sup>a</sup>
$\text{N}_2$	$\text{Zn}_{(6\text{MR})}\text{Al}_{(6\text{MR}-2)}$	0	−41	−3	3	−41	35	−6		
$\text{H}_2$	$\text{Zn}_{(6\text{MR})}\text{Al}_{(6\text{MR}-1)}$	10	−20	−4	7	−17	24	7		
	$\text{Zn}_{(6\text{MR})}\text{Al}_{(6\text{MR}-2)}$	0	−22	−4	8	−18	26	8		
	$\text{Zn}_{(8\text{MR})}\text{Al}_{(8\text{MR}-1)}$	84	−18	−7	13	−12	31	19		
	$\text{Zn}_{(8\text{MR})}\text{Al}_{(8\text{MR}-2)}$	1	−22	−4	8	−18	26	8		
	$\text{Zn}_{(8\text{MR})}\text{Al}_{(8\text{MR}-3)}$	76	−25	−5	8	−22	27	5		

<sup>a</sup> Scaling factor = 0.9928 as explained in the scaling approach in Section S2 in the SI. <sup>b</sup> Experimental values taken from ref. 28.

pronounced for the weakest one,  $\text{H}_2$ , which would further increase the energetic separation between adsorption of  $\text{CO}_2$  or  $\text{N}_2$  and  $\text{H}_2$  adsorption. Consequently, our harmonic calculations provide a conservative estimate of the selectivity among the three adsorbates.

For the CHA framework, Table 2, as well as S7 and S8 in the SI, present the adsorption energies and enthalpies calculated using PBE+D4. To fully understand  $\text{CO}_2$  adsorption in these Zn-CHA samples, all three potentially occurring cation types are investigated. The adsorption energies and enthalpies for  $\text{CO}_2$  and  $\text{H}_2$  adsorbed at all sites, including small (6MRs) and large intersections (8MRs) are exothermic. For the  $\text{Zn}^{2+}$  cation, the calculated adsorption enthalpy of  $\text{CO}_2$  for  $\text{Zn}_{(6\text{MR})}\text{Al}_{(6\text{MR}-2)}$  and  $\text{Zn}_{(6\text{MR})}\text{Al}_{(8\text{MR}-2)}$  are  $−51$  and  $−50$   $\text{kJ mol}^{-1}$ , respectively. While experiments yield a value of  $−42$   $\text{kJ mol}^{-1}$ ,<sup>28</sup> we will later show that this discrepancy is resolved by using the chemically accurate MP2:PBE+D4 approach. Adsorption enthalpies for  $\text{CO}_2$  obtained with other dispersion methods, PBE+TS/HI<sup>86–88</sup> and PBE+MBD,<sup>89</sup> are  $−42$  and  $−49$   $\text{kJ mol}^{-1}$ , respectively, with the former closely matching the experimentally observed adsorption enthalpy, which is in line with literature.<sup>28</sup> Therefore, these findings further suggest that PBE+TS/HI may be used as the preferred generalized gradient approximation (GGA) functional and dispersion combination in future studies of  $\text{CO}_2$  interacting with metal cations in zeolites and other porous materials.

As for the assignment of preferred cation locations, we now calculate C=O stretching vibrations to validate the sites for  $\text{CO}_2$  adsorption present in the experimental samples. To do so, we calculate spectroscopic signatures for  $\text{CO}_2$  adsorbed at different sites and compare them to experimentally measured IR frequencies.<sup>28</sup> The calculated and scaled antisymmetric IR stretching frequencies of  $\text{CO}_2$  adsorbed on  $\text{Zn}^{2+}$  cations located in 6MRs and 8MRs are in a very narrow range from 2348 to 2357  $\text{cm}^{-1}$ . A  $\text{CO}_2$  molecule being adsorbed on a  $\text{Zn}^{2+}$  cation in a 6MR (2357  $\text{cm}^{-1}$ ) most closely aligns with the experimentally

observed frequency of 2356  $\text{cm}^{-1}$ ,<sup>28</sup> which they also assign to  $\text{CO}_2$  adsorption at a  $\text{Zn}^{2+}$  located in a 6MR. However, due to the narrow range of only 9  $\text{cm}^{-1}$  for the calculated IR frequencies, an unambiguous assignment of the  $\text{Zn}^{2+}$  cation location is not possible solely based on this comparison. While the IR spectra might not allow for unambiguous assignment, our chemically accurate calculations for adsorption enthalpies are also in best agreement with experiments when  $\text{Zn}^{2+}$  is in the 6MRs of CHA. Additionally, our calculations indicate that  $\text{Zn}^{2+}$  is energetically most stable in 6MRs. Together, these findings provide compelling evidence for the prevalence of  $\text{Zn}^{2+}$  located in 6MRs in experimental samples.

Similar to FAU,  $\text{CO}_2$  adsorbs more strongly than  $\text{N}_2$ , and both are strongly favoured over  $\text{H}_2$  in cation-exchanged CHA.<sup>90</sup> In the present work, in all sites, there is at least a difference of 20  $\text{kJ mol}^{-1}$  in the adsorption enthalpy between  $\text{CO}_2$  and  $\text{H}_2$  molecules, except for the  $\text{Zn}_{(8\text{MR})}\text{Al}_{(8\text{M}-1)}$  site, at which the difference is only 2  $\text{kJ mol}^{-1}$ . This site, however, is the least stable and will most likely not occur. Consequently, ions located in the 6MRs and 8MRs exhibit selectivity towards  $\text{CO}_2$  adsorption over  $\text{H}_2$ .  $\text{N}_2$  adsorption lies energetically between  $\text{CO}_2$  and  $\text{H}_2$ . It is around 10  $\text{kJ mol}^{-1}$  weaker than  $\text{CO}_2$  adsorption, but about 10  $\text{kJ mol}^{-1}$  stronger than  $\text{H}_2$  adsorption. The same order is retained in the Gibbs free energies of adsorption, which are  $−10$  and  $−6$   $\text{kJ mol}^{-1}$  for  $\text{CO}_2$  and  $\text{N}_2$ , respectively, whereas  $\text{H}_2$  adsorption remains endergonic with a positive free energy of +8  $\text{kJ mol}^{-1}$ . These results suggest that even in a nitrogen-containing atmosphere,  $\text{CO}_2$  will preferentially adsorb at  $\text{Zn}^{2+}$  sites in zeolite CHA.

For  $\text{Zn}(\text{OH})^+$  in CHA, Table S7 in the SI shows the heats of adsorption for  $\text{CO}_2$ , which fall within the range of  $−38$  to  $−43$   $\text{kJ mol}^{-1}$ . The adsorption is weaker at most of these sites compared to  $\text{Zn}^{2+}$  sites. This can be attributed to the reduced accessibility of  $\text{Zn}^{2+}$  cations in  $\text{Zn}(\text{OH})^+$  compared to bare  $\text{Zn}^{2+}$ , which is reflected in the distances between  $\text{Zn}^{2+}$  and  $\text{CO}_2$ . The Zn–(O=C=O) distance in  $\text{Zn}(\text{OH})^+$  is 3.0 Å, and thus



significantly longer than the corresponding distance in Zn<sup>2+</sup>-containing CHA, which is only 2.2 Å. As Zn(OH)<sup>+</sup> only resides in 8MRs, CO<sub>2</sub> interacting with such species is also located in 8MR, which is consistent with experimental findings.<sup>28,91</sup>

To provide a complete picture of the adsorption process, our calculations suggest, in accordance with the literature,<sup>28</sup> that adsorption of CO<sub>2</sub> occurs first at Zn<sup>2+</sup> sites, which are preferably located in 6MRs. Only when all these sites are occupied, CO<sub>2</sub> starts interacting with Zn(OH)<sup>+</sup> sites that are located in 8MRs. Table S8 in the SI presents the adsorption enthalpies of CO<sub>2</sub> in CHA and compares adsorption at all three cationic species (Zn<sup>2+</sup>, Zn(OH)<sup>+</sup>, and H<sup>+</sup>). Adsorption of CO<sub>2</sub> at the most stable BAS sites is weaker than at the most stable Zn<sup>2+</sup> and Zn(OH)<sup>+</sup> sites by 13 (6MR) and 14 kJ mol<sup>-1</sup> (8MR), respectively. These findings imply that CHA with a higher number of Zn<sup>2+</sup> cations in 6MRs is desirable for increasing the CO<sub>2</sub> adsorption capacity, and that the formation of Zn(OH)<sup>+</sup> species and BASs should be minimised for gas adsorption and separation purposes.

**4.2.2. Zn-based MOFs (Zn-MOF-74 and CALF-20).** To explore the interaction of CO<sub>2</sub> and H<sub>2</sub> with Zn<sup>2+</sup> as a framework cation in different MOFs, we investigate Zn-MOF-74 and CALF-20. These frameworks are chosen due to their industrial importance for CO<sub>2</sub> capture from the flue gas post-combustion process.<sup>30,92-99</sup> Fig. 2 and 3 show the optimised structures for Zn-MOF-74 and CALF-20, respectively. The calculated adsorption characteristics for Zn-MOF-74 and CALF-20 are given in Table 3. In the case of Zn-MOF-74, using PBE+D4, the adsorption energies obtained for CO<sub>2</sub> and H<sub>2</sub> are -27 and -7 kJ mol<sup>-1</sup>, and the corresponding adsorption enthalpies for CO<sub>2</sub> and H<sub>2</sub> are -19 and -3 kJ mol<sup>-1</sup>, respectively. The experimental adsorption enthalpies for CO<sub>2</sub> are -30 and -9 kJ mol<sup>-1</sup> for H<sub>2</sub>.<sup>100-102</sup> This reveals an 11 kJ mol<sup>-1</sup> underestimation of the experimental enthalpy by PBE+D4 for CO<sub>2</sub> adsorption and of 6 kJ mol<sup>-1</sup> for H<sub>2</sub>. Conversely, in CALF-20, the computed adsorption energy for CO<sub>2</sub> is -45 kJ mol<sup>-1</sup> and the enthalpy is -37 kJ mol<sup>-1</sup>, closely aligning with the experimental adsorption enthalpy of -39 kJ mol<sup>-1</sup>.<sup>30</sup>

The experimental and calculated adsorption enthalpies suggest that the adsorption of CO<sub>2</sub> is stronger in CALF-20 than in MOF-74. There are several potential reasons for the difference in adsorption enthalpies. The pore size of Zn-MOF-74 is much bigger (8.58 Å)<sup>103</sup> than that of CALF-20 (4.3 Å)<sup>51</sup> which hints at the role of dispersion interactions. CALF-20 exhibits a dispersion contribution to the PBE+D4 adsorption energy for CO<sub>2</sub> of

-38 kJ mol<sup>-1</sup> (84% of total adsorption energy), which is substantially larger than the -13 kJ mol<sup>-1</sup> (48% of total adsorption energy) obtained for Zn-MOF-74. This difference in contributions to the adsorption energy might explain the strongly varying accuracy of the used DFT functional when compared to experiments.

Even though the Zn<sup>2+</sup> cation is more accessible in Zn-MOF-74 and CO<sub>2</sub> can interact more directly with the cation (as shown in Fig. 2, Zn-(O=C=O) bond distance is 2.6 Å), than in CALF-20 (as shown in Fig. 3, Zn-(O=C=O) distance is 3 Å), the better fit and tighter confinement in the latter framework, result in a stronger adsorption. The enhanced adsorption in CALF-20 is primarily governed by dispersion, rather than direct interactions between CO<sub>2</sub> and the Zn<sup>2+</sup> sites.<sup>104-106</sup> Additionally, for CALF-20, the adsorption structure shows that the oxygen atoms of the CO<sub>2</sub> molecule form weak hydrogen bonds with the framework hydrogen atoms (see Fig. 3(a)), which is not the case for MOF-74.

The Gibbs free energies for CO<sub>2</sub> and H<sub>2</sub> adsorption in both MOFs are positive, suggesting that adsorption is thermodynamically unfavourable under standard conditions. Therefore, either increasing the pressure or lowering the temperature is required to promote adsorption. Furthermore, when comparing the investigated MOFs with the zeolites, the Zn-based MOFs exhibit weaker adsorption strengths.

### 4.3. MP2 quality adsorption enthalpies and comparison to experiment

Overall, the PBE+D4 adsorption enthalpies deviate from the experimental heats of adsorption by up to 11 kJ mol<sup>-1</sup>. This suggests that adsorption is already fairly well described with DFT in the investigated materials. Still, a significant improvement is observed with the hybrid MP2:PBE+D4 approach. Fig. 2 and 3, as well as S1 and S2 in the SI, show the cluster models used for the QM:QM calculations, with details described in Section S1 in the SI. The adsorption energies, enthalpies, and Gibbs free energies obtained for CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub> using the hybrid MP2:PBE+D4 approach are shown in Table 4.

The MP2:PBE+D4 adsorption enthalpies align with the PBE+D4 trend in adsorption strength: CO<sub>2</sub> adsorbs most strongly, followed by N<sub>2</sub>, with H<sub>2</sub> binding most weakly. However, the MP2:PBE+D4 Gibbs free energies of adsorption, which ultimately determine adsorption equilibria, alter this ordering in Zn-CHA. In this zeolite, N<sub>2</sub> adsorption (-7 kJ mol<sup>-1</sup>) becomes more exergonic than CO<sub>2</sub> adsorption (-4 kJ mol<sup>-1</sup>). From the perspective of selective CO<sub>2</sub> adsorption and carbon capture applications, preferential N<sub>2</sub> adsorption is undesirable in nitrogen-containing environments. In contrast, for Zn-FAU the MP2:PBE+D4 Gibbs free energies predict exergonic CO<sub>2</sub> adsorption (-6 kJ mol<sup>-1</sup>), while adsorption of N<sub>2</sub> and H<sub>2</sub> is endergonic, with values of 2 and 12 kJ mol<sup>-1</sup>, respectively. This indicates that Zn-FAU is a promising material for selective CO<sub>2</sub> separation, not only from H<sub>2</sub> but also in N<sub>2</sub>-containing atmospheres.

Comparison with experiment shows that for Zn-CHA, the CO<sub>2</sub> adsorption enthalpy calculated using PBE+D4 is

**Table 3** Calculated adsorption energies ( $E_{\text{ad}}$ ) and enthalpies ( $H_{\text{ad}}$ ) at 298 K for CO<sub>2</sub> and H<sub>2</sub> adsorption in Zn-MOF-74 and CALF-20, obtained using PBE+D4. Also reported are zero-point energy corrections ( $\Delta E_{\text{ZPE}}$ ), thermal contributions ( $\Delta E_{\text{therm}}$ ), entropy contributions ( $-T\Delta S_{\text{ad}}$ ), and relative Gibbs free energies ( $G_{\text{ad}}$ ), all in kJ mol<sup>-1</sup>, at a pressure of 0.1 MPa

Framework	Adsorbate	$E_{\text{ad}}$	$\Delta E_{\text{therm}}$	$\Delta E_{\text{ZPE}}$	$H_{\text{ad}}$	$-T\Delta S_{\text{ad}}$	$G_{\text{ad}}$
Zn-MOF-74	CO <sub>2</sub>	-27	2	6	-19	29	10
	H <sub>2</sub>	-7	-1	5	-3	16	13
CALF-20	CO <sub>2</sub>	-45	2	6	-37	46	9
	H <sub>2</sub>	-13	-2	6	-9	23	14



**Table 4** Calculated adsorption energies ( $E_{\text{ad}}^{\text{MP2}}$ ), enthalpies ( $H_{\text{ad}}^{\text{MP2}}$ ), and relative Gibbs free energies ( $G_{\text{ad}}^{\text{MP2}}$ ), all in  $\text{kJ mol}^{-1}$ , at a pressure of 0.1 MPa at 298 K for  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{H}_2$  adsorption in Zn-FAU, Zn-CHA, Zn-MOF-74, and CALF-20 as obtained with MP2:PBE+D4. Adsorption enthalpies ( $H_{\text{ad}}^{\text{PBE+D4}}$ ) calculated with PBE+D4 and experimental enthalpies ( $H_{\text{ad}}^{\text{exp}}$ ) are also shown

Adsorbate	Framework	Site	$H_{\text{ad}}^{\text{exp}}$	$H_{\text{ad}}^{\text{PBE+D4}}$	$E_{\text{ad}}^{\text{MP2}}$	$H_{\text{ad}}^{\text{MP2}}$	$G_{\text{ad}}^{\text{MP2}}$
$\text{CO}_2$	CHA	II <sup>a</sup>	-42	-51	-51	-46	-4
	FAU	I <sub>a</sub>		-58	-62	-56	-19
	FAU	II <sub>a</sub>		-44	-53	-49	-6
	MOF-74	—	-30	-19	-42	-34	-5
	CALF-20	—	-39	-37	-43	-36	10
$\text{N}_2$	CHA	II <sup>a</sup>		-41	-42	-42	-7
	FAU	II <sub>a</sub>		-39	-40	-41	2
$\text{H}_2$	CHA	II <sup>a</sup>		-18	-19	-15	11
	FAU	I <sub>a</sub>		-20	-16	-13	11
	FAU	II <sub>a</sub>		-18	-18	-14	12
	MOF-74	—	-9	-7	-9	-5	11
	CALF-20	—		-13	-7	-3	20

<sup>a</sup>  $\text{Zn}_{(6\text{MR})}\text{Al}_{(6\text{MR}-2)}$ .

$-51 \text{ kJ mol}^{-1}$ , while MP2:PBE+D4 yields a value of  $-46 \text{ kJ mol}^{-1}$ , which is within chemical accuracy limits to the experimental measurement of  $-42 \text{ kJ mol}^{-1}$ . For Zn-MOF-74, PBE+D4 predicts a  $\text{CO}_2$  adsorption enthalpy of  $-19 \text{ kJ mol}^{-1}$  with a substantially larger high-level correction of  $-15 \text{ kJ mol}^{-1}$ , yielding an MP2:PBE+D4 value of  $-34 \text{ kJ mol}^{-1}$ , which, again, is within chemical accuracy limits to the experimental result of  $-30 \text{ kJ mol}^{-1}$ . In contrast, for CALF-20, the PBE+D4 adsorption enthalpy for  $\text{CO}_2$  is  $-37 \text{ kJ mol}^{-1}$  and already very close to the MP2:PBE+D4 value of  $-36 \text{ kJ mol}^{-1}$ . Both values are in excellent agreement with the experimental result of  $-39 \text{ kJ mol}^{-1}$ . This shows that for CALF-20, PBE+D4 provides good agreement with experiments, whereas it performs much worse for MOF-74, highlighting that even for seemingly similar systems (Zn-containing MOFs) and the same adsorbate ( $\text{CO}_2$ ), DFT can exhibit inconsistent performance and can be inaccurate when compared to experiments. In contrast, MP2:PBE+D4 not only yields chemically accurate adsorption enthalpies, but it does so reliably and consistently for all systems.

The observed energy differences between the PBE+D4 and MP2:PBE+D4 approaches can be attributed to MP2's more accurate treatment of dispersion interactions and metal- $\text{CO}_2$  interactions. The inconsistent discrepancies between DFT predictions and experimental values, as well as the varying high-level (HL) corrections, suggest that the nature of  $\text{CO}_2$  adsorption differs across the MOFs. This is further supported by the differing contributions of dispersion to the PBE+D4 adsorption energies. These findings underscore the limitations of commonly used DFT methods and the importance of going beyond them. While DFT-D may yield good agreement with experiment for some MOFs, it can perform significantly worse for others. This variability highlights why consistency and reliability are just as important as accuracy when making predictions for systems lacking experimental data.

## 5. Conclusions

We employ the chemically accurate MP2:PBE+D4 methodology for periodic systems to investigate  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{H}_2$  adsorption in the  $\text{Zn}^{2+}$ -containing zeolites FAU and CHA, as well as  $\text{CO}_2$  and  $\text{H}_2$  adsorption in the MOFs CALF-20 and Zn-MOF-74. For Zn-CHA, Zn-MOF-74, and CALF-20, our calculated  $\text{CO}_2$  adsorption enthalpies deviate by no more than  $\pm 4 \text{ kJ mol}^{-1}$  from experimental values, placing them within the range of chemical accuracy. This demonstrates that the approach provides reliable and consistent predictions for heats of adsorption. In addition, we provide predictions of adsorption enthalpies for  $\text{CO}_2$  in Zn-FAU,  $\text{N}_2$  in Zn-CHA and Zn-FAU, and  $\text{H}_2$  in Zn-CHA, Zn-FAU, and CALF-20, for which no experimental data are currently available.

Among the tested DFT approaches, PBE+TS/HI shows the best agreement with both experiment and MP2-level results for  $\text{CO}_2$  adsorption in Zn-CHA. However, the accuracy of DFT-D methods varies notably across systems. For example, PBE+D4 performs well for  $\text{CO}_2$  adsorption in CALF-20 but less so for Zn-MOF-74. This inconsistency highlights the importance of high-level methods such as MP2:PBE+D4 for making accurate and reliable predictions. This is particularly important in the absence of experimental data, such as in the screening of new materials.

Our results confirm that  $\text{Zn}^{2+}$  cations are the primary  $\text{CO}_2$  adsorption sites in zeolites, with a strong preference for incorporation into 6-membered rings. The preferred binding sites are determined by the local coordination environment of the cation rather than the positions of Al atoms in the framework. This independence from the Al positions contrasts with the behaviour observed for protons forming BASSs. The preferred  $\text{Zn}^{2+}$  locations are supported by the relative stabilities of different adsorption sites, and the good agreement between calculated and experimental  $\text{CO}_2$  adsorption enthalpies and IR spectra.

$\text{CO}_2$  adsorption is generally stronger than that of  $\text{N}_2$ , with both binding significantly more strongly than  $\text{H}_2$ . However, the MP2:PBE+D4 Gibbs free energies of adsorption reverse this preference in Zn-CHA, resulting in stronger  $\text{N}_2$  adsorption. In contrast, for Zn-FAU,  $\text{CO}_2$  adsorption remains exergonic, while adsorption of both  $\text{N}_2$  and  $\text{H}_2$  is endergonic. This renders Zn-FAU a particularly promising material for selective  $\text{CO}_2$  adsorption and carbon capture applications. Moreover, both Zn-FAU and Zn-CHA exhibit  $\text{CO}_2$  adsorption strengths that exceed those of the two MOFs by 10 to 20  $\text{kJ mol}^{-1}$  and may therefore even represent promising competitors to industrial benchmark materials,<sup>28,107</sup> such as zeolite 13X.

## Author contributions

P. P. Samal: writing – original draft, writing – review and editing, investigation, data curation, formal analysis, methodology, validation, visualisation. S. Krishnamurty: supervision, funding acquisition. F. Berger: conceptualisation, writing – original draft, writing – review and editing, investigation,



formal analysis, methodology, validation, supervision, funding acquisition. J. Sauer: conceptualisation, writing – review and editing, supervision, funding acquisition, project administration, resources.

## Conflicts of interest

The authors declare no conflict of interest.

## Data availability

The data supporting this article, including coordinates and example input files, are provided as part of the supplementary information (SI). See DOI: <https://doi.org/10.1039/d5cp04169d>.

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