Combined Nuclear Magnetic Resonance and Molecular Dynamics Study of Methane Adsorption in \( \text{M}_2(\text{dobdc}) \) Metal–Organic Frameworks

Valencia J. Witherspoon,†‡# Rocio Mercado,‡# Efrem Braun,‡ Amber Mace,‡* Jonathan Bachman,‡* Jeffrey R. Long,‡‹ Berhard Blümich,* Berend Smit,§†* and Jeffrey A. Reimer†‡#*

† Department of Chemical and Biomolecular Engineering and ‡ Department of Chemistry, University of California, Berkeley, Berkeley, California 94720, United States
§ Institut des Sciences et Ingénierie Chimiques, Valais, École Polytechnique Fédérale de Lausanne (EPFL), Rue de l’Industrie 17, CH-1951 Sion, Switzerland
† Institut für Technische und Makromolekulare Chemie (ITMC), RWTH Aachen University, 52062 Aachen, Germany
¶ Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

ABSTRACT: We examine the diffusion of methane in the metal–organic frameworks \( \text{M}_2(\text{dobdc}) \) (\( \text{M} = \text{Mg, Ni, Zn} \); dobdc \( ^\ominus = 2,5\)-dioxido-1,4-benzenedicarboxylate) as a function of methane loading through a combination of nuclear magnetic resonance and molecular dynamics simulations. At low gas densities, our results suggest that favorable \( \text{CH}_4\)–\( \text{CH}_4 \) interactions lower the free energy barrier for methane hopping between coordinatively unsaturated metal sites and thus enhance the translational motion of methane down the \( c \)-axis. At higher gas densities, \( \text{CH}_4\)–\( \text{CH}_4 \) interactions become more significant, \( \text{CH}_4\)–\( \text{CH}_4 \) collisions become more frequent, and the self-diffusion begins to decrease. Finally, we observe that the self-diffusion coefficient of methane is inversely related to the binding energy at the coordinatively unsaturated metal sites, such that diffusion is most rapid in the \( \text{Zn}_2(\text{dobdc}) \) framework.

INTRODUCTION

Metal–organic frameworks (MOFs) are porous, three-dimensional solids consisting of metal nodes connected by organic linkers, and their immense synthetic and topological diversity has rendered them exceptional candidates for the selective capture and separation of small molecules, including carbon dioxide, methane, and xenon. For a number of such materials, known as isoreticular frameworks, it is possible to vary the metal ion and/or linker while maintaining the parent topology, therefore enabling systematic variation of material composition and properties such as pore size.

One such family of isoreticular structures is the \( \text{M}_2(\text{dobdc}) \) frameworks (also known as M-MOF-74; \( \text{M} = \text{Mg, Mn, Fe, Co, Ni, Cu, or Zn} \); dobdc \( ^\ominus = 2,5\)-dioxido-1,4-benzenedicarboxylate; Figure 1), which has been widely studied for applications in gas storage and separation because of the presence of coordinatively unsaturated or "open" metal sites that are able to strongly bind and polarize various gases. Further tailoring of this class of materials to exhibit selective \( \text{CH}_4 \) interactions is of interest for establishing highly efficient adsorptive separation processes for applications in natural gas enrichment and the separation of \( \text{CH}_4 \) from power plant flue gas mixtures, as well as toward the development of alternatives for natural gas storage in transportation vehicles. Motivated by these applications, previous research has investigated the potential of \( \text{M}_2(\text{dobdc}) \) frameworks for the storage and separation of methane and demonstrated that the choice of transition metal can significantly influence the material adsorptive capacity. In particular, the \( \text{Ni}_2(\text{dobdc}) \) analogue displays the highest volumetric methane uptake of 230 v STP/v at 35 bar, followed by \( \text{Mg}_2(\text{dobdc}) \) and \( \text{Zn}_2(\text{dobdc}) \) (200 v STP/v and 188 v STP/v at 35 bar, respectively). Neutron scattering characterization of \( \text{CH}_4 \) adsorption in \( \text{M}_2(\text{dobdc}) \) has shed light on this result, revealing that the primary adsorption site is located directly above the coordinatively unsaturated metal...
centers, whereas a secondary site exists along the c-axis between the primary sites. A tertiary binding site has also been located in the center of the pores for methane and certain other adsorbates. At low pressures, the various M₂(dobdc) analogues exhibit differences in CH₄ uptake that primarily arise because of differences in gas binding energies at the open metal sites.

Computational investigations have also found that the relative binding energy of CH₄ at the open metal sites in M₂(dobdc) (M = Mg, Ni, and Zn) is highest in the Ni analogue, followed by the Mg analogue and finally the Zn analogue, in agreement with experimental results. These studies also report differences in the binding energies associated with the secondary adsorption sites. Further, analysis of spatial probability distributions produced from grand canonical Monte Carlo (GCMC) simulation data have predicted that CH₄ molecules spend a larger fraction of their time near the open metal sites in frameworks with stronger adsorption strengths. However, it was not possible to separate these contributions using that experimental method. Understanding the transport contributions of small molecules in MOFs has in general proven challenging, with few experimental techniques available to assess mass transfer coefficients associated with the intracrystalline regime. In this regime, systematic variations in pore features such as size and metal binding site can greatly influence mass transfer.

**NMR Sample Preparation.** M₂(dobdc) analogues were prepared via the previously reported routes yielding crystal sizes between 10 and 20 μm. For each analogue, the as-synthesized material was activated and transferred to an argon glovebox before being loaded into a valved NMR tube. The samples were then activated again for 12 h at 180 °C and 0.01 mbar. Following activation, the samples were cooled to 40 °C and held at the desired equilibrium pressure for 30 min to an hour before closing the valve on the NMR tube. The sample was then allowed to cool to room temperature and transferred to the NMR probe where it was re-heated to 40 °C for 30 min before data collection.

**NMR Measurements.** A 13 Interval Bi-Polar Pulse Field Gradient Stimulated Echo experiment with z-spoiler was performed with a Bruker AVANCE III 700 MHz spectrometer using a Diff30 insert in the Mic5 Bruker imaging probe, as described previously. Diffusion times ranged from 1 to 2.5 ms, whereas the gradient strength ranged from 0 to 17 T/m in 48 steps. The observed attenuation was processed using a one-dimensional inverse Laplace transformation with Tikhonov regularization as implemented in the Kea Prospa software. The reported experimental Dₜ values are the average of the logarithm mean of the resulting bimodal distributions of the inverse Laplace transforms. Each loading condition was sampled 3–5 times, with error bars representing the standard deviation of these multiple measurements. The longitudinal, or spin–lattice, relaxation rate constant (R₁) was obtained using an inversion recovery pulse sequence (180-recover−90-acquire) and the transverse relaxation rate constant (R₂) was measured by implementing a Carr–Parcell−Meiboom–Gill pulse sequence with spectroscopic acquisitions. For all sample loadings, R₁ was smaller than R₂ and the stimulated echo diffusion rate was significantly greater than both R₁ and R₂. The diffusion time was limited to 2.5 ms because of evidence of potential diffusive diffusion at longer times.

**MD Simulations.** The self-diffusion coefficients were computed for CH₄ diffusion in M₂(dobdc) (M = Mg, Ni, Zn) from MD simulations performed using the large-scale atomic/molecular massively parallel simulator (LAMMPS) MD program. The systems were simulated in the canonical ensemble at loadings corresponding to the equilibrium uptake values as determined from GCMC simulations at pressures...
range from 0.1 to 100 bar and 313 K (Tables S2–S4). After
equilibration for 1 ns, each system was simulated for 10 ns with
a timestep of 1 fs using a Nosé–Hoover thermostat. For
framework–CH₄ interactions, a previously parameterized
density functional theory (DFT)-derived force field was
used. Methane–methane interactions were taken from the
transferable potentials for phase equilibria (TraPPE)
force field. Nonbonding interactions were cut off and shifted
to 12.5 Å, and all unit cells were sufficiently replicated so as to
avoid interaction between periodic replica.

The values of Dₛ for adsorbed CH₄ were computed from
these equilibrium simulations using the Einstein equation,
which relates the self-diffusivity of a molecule to its mean-
squared displacement (MSD). In particular, Dₛ values were
calculated from CH₄ MSDs in each framework in the diffusive
regime (2–100 ps). The MSDs were computed from MD
trajectories using the order-n algorithm described previously.⁴⁰,⁴¹

At the lowest CH₄ loadings considered in this work (≈0.027
CH₄/M²⁺), simulations would consist of boxes containing only
one or two CH₄ molecules if carried out in the same manner as
those simulations at the higher loadings. Such a simulation is
problematic because both the temperature and distribution of
molecules within the pores—six pores per simulation super-
cell—are not well-defined for only a single (or few) particle(s)
per supercell. To address these concerns and to establish that
the Dₛ values at these low densities are better defined,
simulations at the same low CH₄ densities (0.027 CH₄/M²⁺)
were carried out with increasing c-axis lengths, l, of the
simulation supercell (where l ∈ {4, 8, 12, 16, 20, 24, 28, 32}),
and with increasing numbers of CH₄ atoms, N, in the pores (N
or 2N per pore, uniformly distributed, where N ∈ {1, 2, 3, 4, 5,
6, 7, 8}). For each metal framework, the low-density Dₛ
was then extrapolated from the converged value corresponding to
an infinitely long simulation box.

For the lowest density simulations in each M₂(dobdc)
framework, which were more expensive because of their size,
the error bars for the Dₛ values were estimated by dividing each
10 ns trajectory into ten 1 ns trajectories and calculating the
standard deviation of the ten Dₛ values computed for each 1 ns
trajectory. For all higher density trajectories, the error bars for
the Dₛ values were estimated by running three different
simulations at the same set of conditions and calculating the
standard deviation of the three Dₛ values computed for each 10
ns trajectory.

Methane Hopping Rates. In order to estimate the CH₄
hopping rate between the primary and secondary binding sites
in each M₂(dobdc) framework, the average exchange rate was
calculated by counting the number of times a CH₄ molecule
transitioned from a primary binding site (2.8–3.0 Å from the
metal) to a secondary binding site (3.5–3.7 Å from the metal),
or vice versa, per nanosecond of time. The CH₄ distances from
each binding site were determined from the spatial distribution
of CH₄ around the metals; peaks in the CH₄ density
corresponding to the two densest binding sites occurred near
2.9 and 3.6 Å for all three frameworks (see Figures S10–S15 in
the Supporting Information section Methane Binding Site
Analysis for details). A width of 0.2 Å around the peak density
of each binding site was chosen such that the CH₄ binding site
would be unambiguous. If a CH molecule crossed into the
intermediate region (between 3.0 and 3.5 Å), then back to
the same site, this was not counted as an exchange event.

Probability Densities. The probability densities (Figure
S16) of adsorbed CH₄ in all three M₂(dobdc) frameworks
were computed by binning CH₄ positions from the 10 ns
trajectories onto a 0.2 × 0.2 × 0.2 Å³ grid using PEGrid and
plotted in VisIt.⁴³

Free Energy Calculations. To estimate the free energy
barrier for hopping between adjacent metal sites, both down
the c-axis (supercell axis in line with the z-axis for a single unit
cell) and along a given ab-plane (orthogonal to the c-axis), MD
simulations were carried out at loadings of 2–14 CH₄
molecules per pore in each M₂(dobdc) framework. The MD
simulations were run for 10 ns, saving the positions of the
adsorbates every MD cycle.

The positions of the adsorbates in a single pore were
mapped to one unit cell along the c-axis and binned to a 0.4 ×
0.4 × 0.4 Å³ grid. The topology of the free energy landscape
was analyzed using the TuTraSt algorithm.⁴⁴ This algorithm
partitions the free energy grid into potential energy wells and
transition states separating the wells by (1) identifying grid
point coordinates of energy minima, (2) growing these
subsequently with increasing energy values using a connected
component search, and (3) detecting merging points. This
provides the necessary information to compute the free energy
barriers and estimate Dₛ analytically by applying transition state
theory (Bennett–Chandler method⁴⁵,⁴⁶) for the transitions
along the c-axis and within the ring. Here, Dₛ along the c-axis
indicates a “true” diffusion of the CH₄ traveling through the
material, whereas the Dₛ for the “ring-like” diffusion does not.

To test the hypothesis that the presence of a CH₄ lowers the
energy barriers for CH₄ diffusion in surrounding diffusion
channels parallel with the c-axis, we compare the potential
energy surface (PES) of CH₄ within the field of the framework
alone and with that with a CH₄ particle placed at a primary
adsorption site. The PES is derived from Monte Carlo
simulations where 100 million single particle insertions are
carried out in the canonical ensemble to sample the energetic
space. The coordinates are saved at every step and treated the
same way as the MD coordinates to create a 3D grid
quantifying the PES. This procedure is first carried out on an
empty framework and from the resulting PES grid, the
coordinates corresponding to the minimum of a potential
energy well of a primary adsorption site are identified, and a
CH₄ particle is positioned at one of these sites within the
framework; the PES is then computed for this derived
framework. The energy barriers for the c-axis transitions are
computed from the two PES grids using the partitioning
algorithm to compare how these are altered in the field of
another adsorbate. The procedure is described in detail in
Mace et al.⁴⁴

RESULTS AND DISCUSSION

NMR relaxation rates of free and adsorbed molecules within an
MOF are determined by fluctuating magnetic fields associated
with molecular motion. Knowledge of the correlation times for
molecular motion, and the origin and magnitude of local
magnetic fields, are thus required to quantitatively model these
relaxation rates. Ignoring chemical shift anisotropy (for
protons this effect is vanishingly small), the fluctuating
magnetic fields driving NMR relaxation derive from time-
varying hetero- and homonuclear dipole interactions, as well as
the coupling of the nuclear spin to the rotational angular
momentum of the molecule. The magnitude of fluctuating
intramolecular dipolar interactions in gas-phase methane has

DOI: 10.1021/acs.jpccl.9b01753
been studied previously\textsuperscript{47,48} and shown to contribute little to NMR relaxation at room temperature. We therefore ignore it henceforth. The coupling of nuclei to molecular rotational angular momentum (the “spin–rotation” interaction\textsuperscript{49,50}) is indeed perturbed by collisions of adsorbed molecules with the walls of porous media and is known to induce NMR spin relaxation (so-called “surface relaxivity,” e.g., for methane in ZIF-8).\textsuperscript{51} This induced relaxation changes with MOF relaxation with changing density, albeit at 193 K.\textsuperscript{52} At low density, our analysis because these data exhibit a maximum in the apparent maximum of our observed relaxation rates $R_1$ (Figure 2, top) with CH$_4$ uptake in M$_2$(dobdc), however, is not consistent with a constant surface relaxivity.

![Figure 2](Figure 2) (Top) Values of the longitudinal relaxation rate, $R_1$, for CH$_4$ adsorbed in M$_2$(dobdc) (M = Mg, Ni, and Zn) as a function of methane loading per coordinatively unsaturated metal site. Interpolated lines are shown as guides for the eye. (Bottom) Exchange rates between the primary and secondary binding sites calculated from MD simulations in each framework. All experiments and simulations were carried out at 313 K. Note the different axes scales for the experimental and simulated data. Error bars are plotted for all points, but in most cases smaller than the markers; for all experimental points, each error bar is the standard error of multiple experiments.

NMR studies of the relaxation of gas-phase methane inform our analysis because these data exhibit a maximum in relaxation with changing density, albeit at 193 K.\textsuperscript{52} At low methane density the relaxation rate correlates with the number of binary collisions,\textsuperscript{47} as the collision frequency increases with pressure, molecular impacts perturb the rotational angular momentum, effectively shortening the rotational correlation time and leading to a maximum in the spin–lattice relaxation rate ($R_1$) as the nuclear Larmor frequency and the collision frequency become equal. At higher pressures, the observed $R_1$ decreases linearly with the gas density because of further shortening of the rotational correlation time. Considering these gas-phase results, we surmise that CH$_4$ exchanges between primary and secondary adsorption sites within M$_2$(dobdc), and/or exchanges between bound and free CH$_4$ decrease the spin-rotational correlation times in a manner similar to gas-phase collisions in the low-density regime, thereby yielding a relaxation rate maximum.

Figure 2 (top) shows that the observed $R_1$ in M$_2$(dobdc) initially increases with increasing density at low pressures and then decreases. Whereas in pure gas a collision is the only interaction strong enough to interrupt the rotational trajectory of a molecule, for confined CH$_4$ at low density the angular momentum is more likely to be interrupted by adsorption at the metal site, that is, the initial binding of the gas molecules directly above the coordinatively unsaturated metal sites.\textsuperscript{16,17} For M$_2$(dobdc) (M = Mg, Ni, Zn), at pressures below 10 bar in all three metal frameworks, the primary sites remain undersaturated, and the probability of finding a molecule at a coordinatively unsaturated metal site is still higher than the probability of finding it elsewhere in the pore. According to GCMC simulations, the coordinatively unsaturated metal sites remain unoccupied (<1 CH$_4$/M$^2$) until approximately 10–20 bar, depending on the framework (Tables S2–S4; Mg: 20 bar, Ni: 10 bar, and Zn: 20 bar). In this low-pressure regime, rotational diffusion is mainly influenced by CH$_4$ hopping between the coordinatively unsaturated metal sites, that is, the free energy barrier for translational motion. This phenomenon has been observed for adsorbed liquid species and is often referred to as reorientations mediated by translational displacements.\textsuperscript{53}

With increasing CH$_4$ loading in each framework, $R_1$ passes through a maximum that can be inversely correlated with the binding energy of the gas at a given metal site—that is, for the framework with the largest metal site binding energy, Ni$_2$(dobdc), a maximum occurs at a loading of ~0.2 CH$_4$ per metal site, followed by maxima at loadings of ~0.15 and ~0.09 CH$_4$ per metal site in the Mg and Zn analogues, respectively (Figure 2). The maximum values of relaxation rates $R_1$ were determined to be approximately 26.1, 25.4, and 24.4 Hz in Ni$_2$(dobdc), Mg$_2$(dobdc), and Zn$_2$(dobdc) at 40 °C, and also correlate with relative methane adsorption enthalpies in each framework. For reference, the adsorption enthalpies at a loading of 0.2 CH$_4$/M$^2$ are 21.0, 18.6, and 16 kJ/mol for Ni$_2$(dobdc), Mg$_2$(dobdc), and Zn$_2$(dobdc), respectively.\textsuperscript{10,54} Thus, the loading at the maximum $R_1$ and the magnitude of the observed $R_1$ maximum, trend with adsorption enthalpy.

The exchange rate between primary and secondary binding sites was also calculated as a function of CH$_4$ per metal site from MD simulations (Figure 2, bottom). Here, the primary binding site was defined as being at a distance of 2.8–3.0 Å from the metal and the secondary binding site was defined as 3.5–3.7 Å away from the metal. At the lowest loadings—between 0.01 and 0.16 CH$_4$/M$^2$—the simulated exchange rates initially decrease significantly for all three frameworks, a trend which is not experimentally observed. For low to moderate loadings, the trend in the calculated exchange rates is in closer agreement with experimental measurements—that is, exchange between the two sites is in general fastest in the Ni$_2$(dobdc) framework and slowest in the Zn$_2$(dobdc) framework under nearly all conditions. Also in agreement with experiments, we found that the exchange rate between the primary and secondary binding sites in simulations is greatest in Ni$_2$(dobdc) and smallest in Zn$_2$(dobdc). For loadings greater than 0.16 CH$_4$/M$^2$, the simulated exchange rates steadily increase in all three frameworks before decreasing again beyond loadings of 0.8 CH$_4$/M$^2$.

Interestingly, we find that in simulations the exchange rate decreases at very low CH$_4$ loadings, although self-diffusion is increasing at these same loadings. The only way there could be...
less exchange events at these loadings would be if the methane molecules remained (on average) a fixed or nearly-fixed distance from the metal site for longer periods throughout their trajectories. As such, a possible explanation for the initial decrease in the exchange rate is that as the number of methane molecules at the primary binding sites increases at very low loadings, any other methane molecules in the pores then take trajectories “around” the primary adsorbed methane molecules (along the minimum free energy path proposed herein). This explanation is supported by the histograms in Figures S11, S13, and S15 in the Supporting Information, which correspond to uptakes of 0.1–0.25 CH4/M2+ (where exchange events are minimized) and show how methane molecules in the simulations spend a maximum of their time at a distance of 3.7 Å away from the metals (slightly farther than the center of the secondary binding sites) in all three frameworks.

Analysis of the pulsed field gradient NMR data (Figure 3, top), revealed self-diffusion coefficients associated with the existence of two populations of CH4—one that experiences fast diffusion (≈10−7 m2/s) and one that undergoes much slower diffusion (≈10−9 m2/s). We propose that the fast self-diffusion measured via NMR can be attributed to the (faster) exchange between adsorbed and intercrystalline CH4 whereas the slow diffusion can be attributed to movement of CH4 within a single crystallite. We note that all analogues of M2(dobdc) possess small crystal sizes—approximately 10 μm in length and a few microns in width for the as-synthesized powders—such that the diffusive path of a molecule can be hundreds of microns in length in a 2.5 ms experimental diffusion time.

The Ds coefficients calculated from simulation in M2(dobdc) are shown in Figure 3 (bottom). We found that the diffusion coefficient increases in magnitude at the lowest uptakes, peaks at an uptake of 0.17 CH4/M2+, and then decreases again. The initial increase in Ds at low CH4 loadings arises from a decrease in the free energy barrier for hopping between open metal sites, as calculated using MD simulations (Figure 4, top).

![Figure 3](image.jpg)

Figure 3. (Top) Experimental values of the methane self-diffusion coefficient, Ds, in M2(dobdc) (M = Mg, Ni, and Zn) as measured by NMR for 2 ms diffusion times. The larger Ds values are attributed to intercrystalline diffusion, whereas the smaller values are attributed to intracrystalline diffusion. (Bottom) Simulated Ds values obtained from 1 ns MD trajectories. Note the different axes scales. Error bars are plotted for all points, but in most cases smaller than the markers; for all experimental points, each error bar is the standard error of multiple experiments.

Whereas it is well known that the binding enthalpy of CH4 increases in the presence of additional CH4 molecules because of favorable methane—methane interactions (Table S5), it is not straightforward that this should be accompanied by a decrease in the free energy barrier for translational motion. At all loadings examined in the simulations, the magnitudes of the intracrystalline Ds are greatest in Zn2(dobdc), followed by Mg2(dobdc) and Ni2(dobdc) (Figure 3, bottom; Figure 4, bottom). On the other hand, experimental measurements at low uptakes show that the magnitudes of the intracrystalline Ds were greatest in Mg2(dobdc), followed by Zn2(dobdc) and Ni2(dobdc). Nonetheless, the overall trend is not surprising, as it suggests that a weaker interaction between CH4 and metal sites (e.g., in the Zn and Mg materials) allows for faster translational motion. These results are in agreement with the relaxation behavior, which indicates that rotational diffusion is mediated by frequent translational displacements.

In order to investigate whether Ds would increase after saturation of all the primary binding sites, we also carried out MD simulations where the number of CH4 molecules per unit cell exceeded that of the open metal centers. As mentioned above, we found that the intracrystalline Ds value increases for uptakes between 0.01 and 0.2 CH4/M2+ (corresponding to pressures ranging from 0.1 to 1 bar) and reaches a maximum at a value of ≈10−8 m2/s before decreasing gradually with increasing uptake (Figure 3, bottom).
Both the NMR data and simulations reveal that the magnitude of $D_1$ is inversely related to the binding energy at the coordinatively unsaturated metal sites ($U_{\text{binding}}$: Ni > Mg > Zn)—that is, self-diffusion is fastest in Zn$_2$(dobdc) and Mg$_2$(dobdc) and slowest in Ni$_2$(dobdc). We also observe that the CH$_4$ heat of desorption increases with increasing CH$_4$ uptake in this regime. However, as can be seen from Figure 3 (bottom), the $D_1$ coefficients initially increase in all three metal frameworks at very low loadings (<0.16 CH$_4$/M$^2$). 

This increase can be explained by considering the free energy barriers between two metal sites. Because CH$_4$ diffuses down the pore by hopping along nearby metal sites, diffusion may occur down the c-axis or in a “ring-like” fashion along a given ab-slice. However, only a lower free energy barrier between two primary adsorption sites located along the c-axis will lead to a greater $D_1$ coefficient: lower free energy barriers along the ring lead to negligible translational motion. We have calculated this free energy barrier from the MD trajectories and indeed found that having more CH$_4$ molecules in the pores lowers the free energy barrier for CH$_4$ hopping between open metal sites along the c-axis at low loadings (Figure 4, top).

To illustrate how, at very low loadings, the presence of a second CH$_4$ molecule lowers the free energy barrier for CH$_4$ hopping from one metal site to another, we have calculated the free energy profiles from simulations with and without a rigid CH$_4$ already bound at the open metal site (Figure 5). The values of the free energy at the corresponding transition states from these simulations are given in Table 1. Indeed, we observe that for transitions at angles $|\rho| = \pi/3$, the free energy barrier is lower in all three frameworks. Figure 6 zooms in on the free energy barriers for transitions along the c-axis at angles $|\rho| = \pi/3$, illustrating how the two free energy wells meet first in the Ni framework, followed by the Mg framework, and finally the Zn framework; it also illustrates further how the free energy is overall lower when there is already a CH$_4$ bound at the open metal site.

One might hypothesize that the sharp increase in $D_1$ at low loadings could be due to more CH$_4$ in the pores effectively blocking the metal sites, thus shielding other CH$_4$ molecules from these strong binding sites and allowing them to diffuse past without binding. However, probability density maps show that the CH$_4$ spends most of its time above the metal sites in simulations at both of these densities (Figure S16), and in fact the results at both densities look very similar, thus eliminating this as a possible mechanism.

Although the magnitudes of the diffusivities calculated from simulations differ by an order of magnitude from the pulsed field gradient measured values, trends between the two are remarkably similar. For example, Ni$_2$(dobdc) exhibits the slowest diffusion, and Zn$_2$(dobdc) and Mg$_2$(dobdc) have about the same diffusivities in both simulation and experiment. In both experimental and simulation data, there is an initial rise in diffusivity with increasing CH$_4$ uptake. These initial increases are rationalized by considering the growing presence of CH$_4$ molecules in the pores where, at low densities, they serve to stabilize the transition states for hopping from one metal site to another. At the high uptakes not accessible with NMR, the simulations show how decreasing diffusivity is a result of an increasing frequency of methane–methane collisions within the pores that leads to a decrease in CH$_4$ MSD.

As discussed in the Methods section, at the lowest CH$_4$ loadings considered in this work (~0.027 CH$_4$/M$^2$), simulations would consist of boxes containing only one or two CH$_4$ molecules if carried out in the same way as the simulations at the higher loadings, which would be problematic from the simulation point of view. As such, various fixed-density simulations were carried out that would allow us to extrapolate to an infinitely large simulation box. From these constant-density simulations at low uptakes, we find that as the number of molecules in the simulation box increases at a fixed density, the self-diffusion coefficients slowly increase until converging, as illustrated in Figure 7.

The magnitude of $D_1$ converges faster for simulations involving 2N CH$_4$ atoms per compared to N CH$_4$ atoms.
per pore, as expected. As shown by the y-intercepts of the linear fits in Figure 7, which extrapolate the diffusion coefficient to an infinitely long simulation box, the value of $D_s$ is greatest in the Zn framework and smallest in the Ni framework at low CH$_4$ densities ($D_s$: $1.27 \times 10^{-8}$, $1.03 \times 10^{-8}$, and $1.34 \times 10^{-8}$ m$^2$/s for Mg, Ni, and Zn, respectively). This trend is also in agreement with that found for $D_s$ from simulations at larger densities (Figure 3), as the overall magnitude of $D_s$ is found to be inversely related to the CH$_4$ binding energy at the coordinatively unsaturated metal sites (Table 2).

### CONCLUSIONS

We have used a combination of NMR and computational studies to elucidate a relationship between the strength of CH$_4$ binding at the coordinatively unsaturated metal sites in M$_2$(dobdc) ($M = \text{Mg, Ni, and Zn}$) frameworks and the dynamics of adsorbed CH$_4$. MD simulations were particularly key to fully understanding the diffusion of CH$_4$ at low and high densities that are not easily accessible in NMR experiments.

From NMR experiments, we observed a maximum in the spin−lattice relaxation rate $R_1$ of adsorbed methane gas, which we attributed to the influence of exchange between primary and secondary adsorption sites on the characteristic rotational correlation time of CH$_4$. We demonstrated this in an isoreticular MOF series in which the strength of interaction between CH$_4$ and the coordinatively unsaturated metal sites dictates changes in exchange rates. These findings support the continued use of loading-dependent relaxometry studies to discern differences in surface interactions between adsorbates and adsorbent.

Table 2. Methane Densities in Molecules per Å$^3$ Used in the Low-Density Simulations

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>Ni</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>N molec per Å$^3$ ($\times 10^{-4}$)</td>
<td>2.99</td>
<td>3.05</td>
<td>3.04</td>
</tr>
<tr>
<td>2N molec per Å$^3$ ($\times 10^{-4}$)</td>
<td>5.98</td>
<td>6.10</td>
<td>6.08</td>
</tr>
</tbody>
</table>

"In these simulations, the number of CH$_4$ molecules and number of unit cell replicas were varied, but the densities remained the same. A density of $N$ molecules per Å$^3$ corresponds to a value of 0.027 CH$_4$/M$^{2+}$ in all three M$_2$(dobdc) frameworks, and a density of 2N molec per Å$^3$ corresponds to a value of 0.055 CH$_4$/M$^{2+}$ in all three M$_2$(dobdc) frameworks."
maximum in all three structures; we attribute this increase to a stabilization of the free energy barrier for CH$_4$ hopping between two open metal sites because of the presence of additional CH$_4$ molecules. This result is interesting because the binding enthalpy of CH$_4$ in M$_2$(dobdc) also becomes more favorable as more methane adsors in the framework (at low densities); however, this does not lead to CH$_4$ becoming more localized because of the simultaneous stabilization of the free energy barrier for hopping between open metal sites along the c-axis. This increase in $D_s$ is only noticeable until a loading corresponding to a single CH$_4$ molecule per six metal sites, where the $D_s$ values are maximized.

At very low CH$_4$ loadings (~0.027 CH$_4$/M$^{2+}$), simulations of CH$_4$ in M$_2$(dobdc) were carried out in increasingly larger and larger simulation boxes (keeping the CH$_4$ density in the pores fixed) to show that as we increase the number of molecules in the simulation box while keeping the densities fixed, the self-diffusion coefficients slowly increase until converging at a constant value. We attribute this behavior to an increase in the number of intermolecular collisions at these very dilute densities when there are simply more adsorbents in the simulation box.

Finally, the magnitudes of the intracrystalline CH$_4$ $D_s$ coefficients are overall smallest in Ni$_2$(dobdc) and largest in Zn$_2$(dobdc). This is because the coordinatively unsaturated frameworks interact more strongly with adsorbed CH$_4$ in the Ni$_2$(dobdc) framework and more weakly in the Zn$_2$(dobdc) framework; the stronger a CH$_4$ molecule adsors to the framework, the less distance it can travel over a fixed amount of time. Simulations and experiments are in agreement with the trend in the $D_s$ coefficients predicted at the higher CH$_4$ loadings studied.

We note that none of the computational studies presented here would have been possible without parameterization of the DFT-derived force field reported previously,$^{10}$ illustrating the value of having inexpensive yet accurate models of adsorption in promising nanoporous materials for the comprehensive study of adsorbate thermodynamics. From an experimental standpoint, NMR facilitates a valuable systematic study of the effect of host–guest energetics on adsorbate diffusion in MOFs. The comprehensive and improved understanding of adsorbate behavior at the atomic scale using these complementary techniques reinforces the concept that combined experimental–computational studies can be very valuable in guiding the improved design of materials for gas separation applications, especially when seeking to understand adsorption and diffusion behavior at the atomic scale.

### ASSOCIATED CONTENT

* Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.9b01733.

- Simulation structures; GCMC simulation details; MSD$_3$; self-diffusion coefficients; methane binding site analysis; probability densities; and example experimental data (PDF)

### AUTHOR INFORMATION

*Corresponding Author*

E-mail: reimer@berkeley.edu.

**ORCID**

Valencia J. Witherspoon: 0000-0002-2718-6605

### ACKNOWLEDGMENTS

This work was supported as part of the Center for Gas Separations Relevant to Clean Energy Technologies, as an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award DE-SC0001015. V.J.W. and R.M. acknowledge support by the National Science Foundation under both grant numbers DGE 1752814 and DGE 1106400. This research also used resources of the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under contract no. DE-AC02-05CH11231. We also thank ACaNet, the Aachen-California Network of Academic Exchange (DAAD Germany), for supporting the research visit of V.J.W. to RWTH Aachen University, and Dr. Katie R. Meihaus for editorial assistance.

### REFERENCES


