Molecular Level Investigation of CH₄ and CO₂ Adsorption in Hydrated Calcium–Montmorillonite

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Supporting Information

ABSTRACT: We have studied the mechanism of intercalation and methane adsorption from a $H_2O/CH_4/CO_2$ mixture on a prototypical swelling shale component, Ca-montmorillonite. We employed ab initio molecular dynamics simulations at 323 K and 90 bar to obtain molecular level information on adsorption energetics, speciation, and structural and thermodynamic properties. Interaction of CH₄ with surface Lewis acidic sites (Ca²⁺, surface OH) results in large induced dipoles $(\sim 1 \text{ D})$ that lead to relatively strong adsorption energies compared to interactions of the normally apolar CH4 that level off once a CH₄ layer is formed. Intercalated CH₄, also exhibits large induced dipoles at lower hydration levels, when the interaction with $\hat{C}a^{2+}$ cations are less hindered. CO₂ displaces CH₄ in the coordination sphere of the cations (in the



interlayer) or on the surface, thereby driving CH_4 extraction. Our simulations indicate that there is an optimal pressure range $(\sim 70-90 \text{ bar})$ where scCO₂-facilitated CH₄ extraction will be maximized.

1. INTRODUCTION

The global demand for energy has accelerated the development of low-cost technologies for utilization and monetization of anthropogenic CO₂ emitted from coal-burning power plants.^{1–6} Enhanced oil recovery (EOR) is of particular interest as more than 50% of fuel still remains underground after the primary extraction.⁷ Geologic carbon sequestration (GCS), comprising of injecting supercritical CO₂ (scCO₂) into underground reservoir rocks in the form of a compressed liquid, ^{8–10} has been entertained as a method for secondary EOR $^{7,11-15}$ Shale minerals form low permeable caprock, which can be used to store CO2.¹⁶ Shale gas is an unconventional natural gas resource largely composed of methane.¹⁷ Utilization of CO₂ to produce additional methane from depleted fractured shale gas reservoirs offers another economic driver with the added benefit of creating a long-term greenhouse gas storage option.¹⁸⁻²² In addition, shale gas formations rich in clay minerals and organics are often strategically located near large stationary CO₂ point sources in the U.S.^{23,24} However, realizing the potential of this unconventional storage resource requires a much better understanding of gas sorption processes and the dominant interactions between CH4, CO2, H2O, and the primary minerals and organic phases in shales.

Montmorillonite (MMT) is a swelling clay consisting of 2:1 phyllosilicate layers of octahedrally coordinated Al³⁺, between two tetrahedral silicate layers, often referred to as T-O-T. It carries a net negative charge, which is compensated by interlayer cations such as Na⁺, K⁺, or Ca^{2+,25-27} Intercalation of extrinsic species depends on interlayer cations, relative humidity, and heterogeneity of the native interlayer species. The intercalation process involves solvation of interlayer cations, ion exchange and interaction between cation and the different species in the interlayer.²⁸ Studies on the intercalation and swelling behavior of hydrated clay minerals show that the interlayer structure with different cation is subject to different hydration mechanisms.²⁹⁻³⁹ Liu et al. studied adsorption of methane on Ca-montmorillonite, kaolinite, and illite over a pressure range of 0-18.0 MPa at 60 °C, where they observed the highest adsorption capacity in Ca-MMT.⁴⁰ They also showed that CH4 was adsorbed both on the external surface and interlayer space of MMT in contrast to kaolinite and Illite where CH₄ adsorbs only on the external surface. Experimental studies by Guggenheim et al. and Seo et al. showed that the intercalation of methane molecules into clay interlayers resulted in formation of methane hydrates at certain temperature and pressure conditions.^{41,42} There have been extensive theoretical studies on methane sorption in hydrated smectite using molecular dynamics (MD) and Monte Carlo (MC) simulations showing that methane hydrate formation can occur within the interlayer.43-48 In addition, Rao et al. found that initial clay swelling is dominated by water intercalation, followed by the intercalation of methane using grand-canonical Monte Carlo

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(GCMC) and MD simulations.^{47,48} The swelling of clay is also affected by incorporation of CO_2 in the interlayer. Schaef et al.⁴⁹ and Loring et al.⁵⁰ observed the expansion of interlayer space in Ca–MMT by exposing to variably wet scCO₂, also seen by Giesting et al.⁵¹

In a recent computational study of Ca-rich MMT,⁵² it was shown that CO₂ intercalation causes further interlamellar expansion in sub- to 1W and 2W systems. The computed spacings are consistent with both computational³⁹ and experimental findings^{31,49} in the Ca–MMT system. Additionally, it is reported that a metastable structure associated with the 2W state after being exposed to scCO₂ is possible, in agreement with some older experimental observations.⁴⁹ It was also shown that intercalated, Ca-bound CO₂ molecules at subsingle hydration levels are vibrationally constrained and contribute to a blue-shift in the frequency envelope in the asymmetric stretch compared to scCO2.52 We should point out that although the CO₂ asymmetric stretch in scCO₂ may be red-shifted compared to gaseous CO2, the cation-bound CO2 asymmetric frequency may also be blue-shifted compared to scCO₂^{52,53} and still be red-shifted compared to the gas phase.⁵⁴

Recent subsurface transport simulations by Bacon et al. showed that CO_2 injection enhanced methane desorption by almost a factor of 2.⁵⁵ Combined experimental and *ab initio* molecular simulations of CH_4 and CO_2 sorption on Camontmorillonite, based on the adsorption energy profiles, show that CH_4 and CO_2 have variable pressure dependencies.⁵⁶ Additional adsorption studies of CH_4/CO_2 mixture in variably hydrated Na-montmorillonite using GCMC simulations,^{20–22} show preferential adsorption of CO_2 over CH_4 indicating the potential for secondary methane recovery.

The current work presents a study of the intermolecular interactions between a mixture of $CH_4/H_2O/CO_2$ and Ca-montmorillonite using a dispersion corrected density functional based ab initio molecular dynamics simulations (AIMD). This approach allows us to examine intermolecular interaction and polarization effects on equal footing. We find that the polarization of methane is a critical feature of its adsorption and intercalation in clays. In the context of $scCO_2$ as an extraction fluid, the following critical molecular interactions are at play: (i) The adsorption mechanisms for CO_2 and CH_4 are radically different. While CO_2 displays a higher affinity for Lewis acidic sites in clays, a free energy analysis indicates that a full CO_2 monolayer (pressure >70 bar) is needed to displace CH_4 . (ii) CH_4 interaction with water assists in its mobilization away from the mineral.

2. COMPUTATIONAL DETAILS

We have carried out AIMD simulations to study structural and thermodynamic properties of CH_4 and CO_2 in hydrated Ca– MMT with periodic boundary conditions (3D-PBC). All calculations were performed within the generalized gradient approximation (GGA) with the exchange correlation functional PBE of Perdew, Burke and Ernzerhoff⁵⁷ as implemented in the CP2K package.⁵⁸ Dispersion corrections were taken into account using Grimme's third-generation corrections (DFT-D3) which can describe energies for adsorption processes on ionic surfaces much more precisely.⁵⁹ For the core electrons norm-conserving pseudopotentials are used,^{60,61} while the valence wave functions were expanded in terms of double- ζ quality basis sets optimized for condensed phase systems to minimize linear dependencies and superposition errors.⁶² plane-wave basis set with a 400-Ry cutoff.⁶³ The Γ -point approximation is employed for the Brillouin zone integration because of the significant size of the supercell.

We first performed *NVT* simulations at 323 K with CH₄ and hydrated Ca²⁺ in a CO₂ simulation cell to study how hydration of Ca²⁺ affects dynamics of CH₄ and CO₂ in the system. After optimizing cell parameters and atomic positions with 26 CO₂ in the simulation cell at 90 bar to obtain a scCO₂ structure, we added Ca²⁺(H₂O)_n(CH₄)₂ (n = 2, 4, 6, 8, 10) into the CO₂ simulation cell. This allowed us to obtain good starting configurations of a hydrated calcium cation.⁶⁴ The Ca–MMT model used here was adopted from our recent work⁵² and originated from Vianni's model.⁶⁵ The resulting 2 × 1 × 1 supercell contained two interlayer Ca cations and 4H⁺ within the clay layer. The initial lattice parameters of the supercell were adopted from the work of Berghout et al.,³⁴ a = 10.48 Å, b= 9.03 Å, c = 10.06 Å, $\alpha = 90.9^{\circ}$, $\beta = 99.3^{\circ}$, and $\gamma = 90^{\circ}$, who optimized the cell parameters of various montmorillonites.

To investigate CH_4 harvest from the interlayer, we assume that there are two intercalated CH4 in the system. Then, we examined an array of systems by varying the number of interlayer H_2O and CO_2 molecules, with nH_2O (n = 4, 6, 8, 10, 16) and mCO_2 (m = 0, 4) to study how variation of H₂O and CO₂ content in the interlayer affects CH₄ extraction from the system. Although Schaef et al. showed that CO₂ concentration decreases with increasing H₂O concentration in the system,⁴ most recent experiments by Bowers et al. showed that the maximum mole fraction of $CO_2 (X_{CO_2} = CO_2/CO_2 + H_2O)$ in the interlayer of Ca smectite is ${\sim}0.5$ for both 1W and 2W systems at 50 $^{\circ}C$ and 90 bar. 66 In our study the highest concentration of CO₂ (4H₂O/4CO₂) corresponds to X_{CO_2} = 0.5, which is within this estimated range. For each system, the supercell parameters as well as the atomic positions were fully optimized at P = 90 bar, which was one of the experimental parameters used by Schaef et al.⁴⁹ To determine the local structure, atomic density distributions, and various thermodynamic properties under experimental conditions, we performed DFT-based molecular dynamics simulations within the canonical NVT ensemble at T = 323 K, the temperature used in the experimental studies by Schaef et al.⁴⁹ The simulations were initiated with structures obtained by the cell optimizations at 90 bar using a 0.5 fs time step. Detailed computational methods we employed for the calculations can be find in our previous work.⁵² Trajectories were initially equilibrated by means of a thermostat for about 5 ps, followed by canonical runs of 20-25 ps. Statistical averages were typically collected in the last 15-20 ps of the simulation by examining the convergence of the statistics with different time intervals. The following properties were calculated:

- (a) Density profiles of the interlayer species along the z direction, showing the distribution of each species with respect to the midplane parallel to the clay layers.
- (b) Radial distribution functions (RDF) representing the average distance of any two atomic species α and β :

$$g_{\alpha\beta}(r) = \frac{1}{N_{\alpha}\rho_{\beta}} \sum_{I \in \alpha, J \in \beta} \delta(r - |R_{J} - R_{I}|)$$

Here ρ_{β} is the average density of atoms of species β , and N_{α} corresponds to the number of atoms of species α . Integration of this function gives the coordination number of species β around α .

(c) Infrared (IR) spectra were calculated from the Fourier transform of the autocorrelation of the total dipole moment. The harmonic approximation was used to extract the quantum correction factor that satisfies the fluctuation-dissipation theorem.⁶⁷ The resulting absorption coefficient is defined as

$$\alpha(\omega) \propto \omega^2 \beta \int_{-\infty}^{+\infty} \mathrm{d}t \, \mathrm{e}^{-i\omega t} \langle M(t) \cdot M(0) \rangle$$

where *T* is temperature, $\beta = (k_B T)^{-1}$, *M* is the total dipole moment, and the angular brackets indicate the statistical average over time. The total dipole moment at each time step was evaluated using the Berry-phase approach.⁶⁸ In addition, we calculated the projected vibrational density of states (pVDOS) on each species using velocity autocorrelation function to assign the contribution of different species to the spectra.

(d) Instantaneous molecular dipole moment (D) was obtained using

$$D = \sum_{i=1}^{N} q_i R_i - 2 \sum_{s=1}^{nw} R_s$$

where *N* is the number of atoms in a molecule, q_i is the valence atomic charge of atom *i*, R_i is coordinates of atom *i*, *nw* is number of centers of doubly occupied maximally localized Wannier Functions (MLWFs; *nw* = 4 for H₂O and CH₄, *nw* = 8 for CO₂), and R_s is the coordinates of *s*th maximally localized Wannier center associated with each molecule.^{69,70} To get maximally localized Wannier center calculations implemented in the CP2K package⁵⁸ using 1000 configurations for each system, extracted from *NVT* trajectories.

In addition, we modeled CH₄ surface adsorption on the external Ca-MMT surface using a $2 \times 2 \times 1$ supercell. A vacuum of 15.4 Å was used in the (001) direction to minimize the interaction between adsorbed species and the periodic image of the surface. We kept one Ca cation on the surface and added 4 H⁺ for the charge compensation. After initial optimization of the cell without CH4, we systematically added one CH_4 molecule on the surface up to a total of 16 CH_4 , corresponding to an increase of CH_4 density by 0.00865 g/cm³ at a time. This covered the range of CH4 densities used in experimental measurements,⁵⁶ roughly corresponding to CH₄ pressure (P_{CH_4}) ranging between 0–120 bar. Each system was equilibrated for a short time (\sim 5 ps) at temperatures similar to the experiment and then slowly annealed and optimized to obtain the final energy. In addition, a simulation with just CH₄ at experimental conditions (supercritical, 50 °C, 90 bar) was performed, followed by annealing and optimization to extract an average energy for the scCH₄ system.

The intercalation/adsorption energies at given hydration states were calculated as energy differences based on the following chemical equilibrium:

$$\operatorname{clay}/(\operatorname{H}_2\operatorname{O})_n/(\operatorname{CH}_4)_m + q\operatorname{CH}_4 \rightleftharpoons \operatorname{clay}/(\operatorname{H}_2\operatorname{O})_n/(\operatorname{CH}_4)_{m+a}$$

$$\Delta E_{rxn} = \{E[\operatorname{clay}/(\operatorname{H}_2\operatorname{O})_n/(\operatorname{CH}_4)_{m+q}] \\ -E[\operatorname{clay}/(\operatorname{H}_2\operatorname{O})_n/(\operatorname{CH}_4)_m] - q \times E[\operatorname{CH}_4]\}/q$$

where $E[CH_4] = E[CH_{4(gas)}]$ for $P_{CH_4} < 4.6$ MPa and $E[CH_4] = E[scCH_4]$ for $P_{CH_4} \ge 4.6$ MPa.

3. RESULTS AND DISCUSSION

3.1. $Ca^{2+}(H_2O)_n \cdot (CH_4)_2$ in Supercritical CO_2 . We begin our discussion by examining the intermolecular interactions of a simple prototype: $Ca^{2+}(H_2O)_n(CH_4)_2$ in scCO₂, at 323 K with $2 \le n \le 10$. This allows us to examine Ca^{2+} solvation in a threecomponent fluid without the complexity of the mineral surface. Figure S1 shows an optimized structure of the $Ca(H_2O)_6^{2+}$ system, which is considered a fully saturated first solvation shell for Ca^{2+} at 0 K.⁶⁴ For this complex, all six H_2O molecules lie within 2.2–2.5 Å from Ca^{2+} , while the CH_4 molecules are located on the periphery of the first solvation shell at 3.2 and 3.5 Å from Ca^{2+} . One might expect a similar picture in wet supercritical CO_2 . However, AIMD at T = 323 K shows a different picture; see Figure 1. For the systems with 2 and 4



Figure 1. (a) Radial distribution functions (RDFs) of Ca– O_{H_2O} (green), Ca– C_{CH_4} (blue), Ca– O_{CO_2} (red), and C_{CH_4} – O_{H_2O} (cyan) provides the average distances between a pair of the species. (b) The integral of the RDFs provides estimates of the number of contacts. The same color code applies as in part a.

H₂O, the Ca²⁺-H₂O distance uniformly decreases to \sim 2.3 Å. In all cases, some of water molecules can be found within the second solvation shell. Interestingly, CH_4 can be found within the first coordination sphere for only n = 2. For n = 6, CO₂ molecules become part of the first solvation shell. Calculation of distances between neighboring molecules and Ca²⁺ as a function of time reveals that three H₂O molecules move away from Ca cation while two CO₂ molecules enter the first coordination sphere within 0.5 ps (see Figure S2). By further examination of the molecular dynamics trajectories, we note that the H₂O molecules moving away were initially nearest neighbors to the CH4 molecules and their association continues for the duration of the trajectory. This implies that the presence of CH₄ strongly modifies the Ca²⁺ solvation properties in the system. This behavior persists for higher hydration levels, up to n = 10, see Figure S3. These observations indicate that (i) at low hydration levels, $Ca^{2+}-CH_4$ interactions are present; (ii) at intermediate hydration levels, Ca^{2+} exhibits a mixed H_2O/CO_2 solvation shell, while the first CH₄/H₂O interactions become evident; (iii) compared to systems without $CH_{4,}^{52} Ca^{2+}-CO_{2}$ interactions persist even in the higher hydration levels. This behavior correlates with the interaction energies $(E_{\rm b})$ between Ca^{2+} and the three molecular components, shown in Table S1.

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Figure 2. Cell optimized structure of CH_4 intercalated Ca-MMT with different number of H_2O and CO_2 . 1W/2W denotes number of water layer(s). Blue circles are for Si, gray for Al, red for O, white for H, black for C, and green for Ca.

3.2. Intercalation of H_2O/CO_2/CH_4 in the Ca-MMT at 323 K. *3.2.1. Structural Properties.* We next discuss the effect of CH₄ intercalation on d_{001} expansion in the Ca-MMT. Full cell optimizations of Ca₂(Al₄Si₈O₂₂)₂(OH)₄·2CH₄·nH₂O· mCO_2 with n = 4, 6, 8, 10 and m = 0, 4 at 90 bar were performed with the optimized structures shown in Figure 2. The choice of CH₄ concentration was chosen to represent reported experiment in the literature.⁴⁹ The resulting *d*-spacings and % changes compared with those without CH₄ molecules are given in Table 1, where 1W/2W denote systems with one/ two water layer(s) in the interlayer, following the established term for montmorillonite hydration states.⁵²

Compared to a previous study of Ca–MMT without $CH_{4^{\prime}}^{52,71}$ the presence of CH_4 causes a small to moderate increase in the *d*-spacing with (6.2 to 8.7%) and without CO_2

Table 1. d_{001} Spacing of Montmorillonite Models with two Interlayer Ca Cations, Ca₂(Al₄Si₈O₂₂)₂(OH)₄·2CH₄·*n*H₂O· *m*CO₂, with *n* = 4, 6, 8, 10, 16 and *m* = 0, 4, Representing ~1W and 2W Clay Hydrates^{*a*}

model system	~1W hydrates			~2W hydrates		
no. of CO ₂	no. of H ₂ O	<i>d</i> ₀₀₁	Δd (%)	no. of H ₂ O	<i>d</i> ₀₀₁	$\Delta d.(\%)$
m = 0	n = 4	12.45	11.7	n = 8	14.00	-0.7
	n = 6	12.34	9.3	n = 10	14.20	-0.1
				n = 16	14.71	0.1
m = 4	n = 4	13.06	8.7	n = 8	14.49	9.9
	n = 6	13.44	6.2	n = 10	14.68	9.7/3.4
				n = 16	15.58	4.3

 ${}^{a}\Delta d$ (%) shows the change of *d* spacing in percentage compared with that without CH₄. For the 10H₂O/4CO₂ system two Δd valus are obtained by using values of quasi-1W/2W. The full set of cell-optimized parameters can be found in the Supporting Information, Table S2.

(9.3 to 11.7%) in 1W systems. In contrast, 2W systems without CO_2 maintain nearly the same *d*-spacing ($\leq 0.7\%$), while those with CO_2 exhibit a 3.4 to 10% expansion. At sub- to 1W systems, the interlayer Ca^{2+} ions are coordinated by both surface oxygens and intercalated molecular species, resulting in inner-sphere complexes. H₂O, CH₄ and CO₂ all remain within the first solvation shell of the cations. In the 2W systems, we observe a clear double layer with all Ca^{2+} cations in the middle, forming outer-sphere complexes.

AIMD at T = 323 K (NVT) was performed to examine the distribution on molecular species within the interlayer space. The distribution of species shown along the z-direction is shown in Figure 3, with the vertical dashed lines marking the mineral surface from the middle of the interlayer distance (defined as "0"). The four upper panels in Figure 3 correspond to the ~1W (left) and ~2W (right) models without CO_2 . Water molecules manifest a unimodal distribution for 1W that becomes bimodal for 2W. In all cases, CH₄ can be found in the center of the interlayer space, while solvated Ca cations mostly form inner sphere complexes even for up to eight H₂O moieties, where a dynamic equilibrium exists between inner and outer sphere complex formation. CO_2 intercalation (Figure 3, four lower panels) strongly perturbs the molecular distributions within the layer: (i) The Ca cations form inner sphere mixed coordination complexes, where CO₂ also coordinates the cations, which is also seen in higher number of H_2O ($n \ge 6$) in the system without clay support (see Section 3.1). For the higher hydration levels ($8/10 H_2O$ cases), the Ca cation distribution becomes unimodal, at the center of the interlayer space. (ii) The CH_4 distribution is skewed away from the center following the water distribution. This is indicative of appreciable CH_4/H_2O interactions that further promotes the mixed coordination sphere about Ca²⁺. (iii) As a result, the H₂O distribution becomes asymmetric and multimodal even in the 4/6 H₂O cases.



Figure 3. Atomic density profile of Ca^{2+} (green), O of H_2O (red), C of CH_4 (violet), C of CO_2 (blue), and O of CO_2 (dotted blue) in the interlayers, which shows distribution of atomic species along *z*-direction. The dashed vertical black lines mark the basal O atoms with the origin at the midplane of the interlayer region. For clarity, we omit the H distribution.

To further clarify the local structure of the intercalated species, we calculated the radial distribution function (RDF), Figures 4 and S4, and compared with the simple model shown in Figure 1. In the absence of CO₂, Figure 4 upper four panels, only at the lowest hydration do we find CH₄ within the first coordination shell of Ca²⁺, at ~3.0 Å. As hydration increases,

Figure 4. Radial distribution functions (RDFs) of $Ca-O_{H_2O}$ (green), $Ca-C_{CH_4}$ (blue), $Ca-O_{CO_2}$ (red), and $C_{CH_4}-O_{H_2O}$ (cyan) for 1W (left panel) and 2W (right panel) before and after CO_2 intercalation provide the average distances between any pair of the relevant species. RDF showing Ca contact is given as average values of both Ca cations in these systems.

the average $Ca^{2+}-CH_4$ distance increases to R > 4.0 Å. The $Ca^{2+}-H_2O$ average distances remain about the same (~2.5 Å), although the distributions become broader at higher hydration levels. Upon CO₂ intercalation, the CH₄-H₂O pair distributions become sharper (centered at ~ 3.5 Å), and as the hydration levels increase $(6-10 \text{ H}_2\text{O})$, they are centered between the first and second solvation shell of the Ca²⁺ cations. Here, it is worth noting that a peak at ${\sim}3.5$ Å between C_{CH_4} and O_{H_2O} is a typical distance also observed in studies of methane in bulk liquid water.^{48,72,73} At all hydration levels, CO₂ is part of the first coordination sphere about Ca^{2+} , at ~2.5 Å. Furthermore, the RDF of $Ca^{2+}-CO_2$ shows stronger interactions (shorter distances and larger intensities) compared to systems without CH₄.⁵² The short Ca²⁺-CO₂ distance can be due to higher CO₂ concentrations used in our studies as we are modeling the interactions of clay with water-bearing supercritical fluid. However, the simulation results also indicate that this behavior may be due to the favorable association of CH₄ and H₂O that partially removes waters from the solvation shell of Ca²⁺allowing some CO₂ molecules to move in this space in a manner similar to that observation seen in systems without clay (see discussion in section 3.1). In addition, the RDF of C–O for CO₂ (figure not shown) has a peak at \sim 3 Å which is characteristic of distorted T-shaped pairwise interaction of supercritical CO2 molecules, 52,53,74 indicating CO_2 clustering in the system.

At higher hydration levels, the stronger $Ca^{2+}-CO_2$ interactions combined with the mixed coordination of outer sphere complexes, help drive CO_2 activation. This becomes evident in the observation of HCO_3^- formation resulting from H_2O addition to a Ca-coordinating CO_2 , see Figure 5. H⁺ from the broken water moves to the surface. We note that the formation of Ca^{2+} outer sphere complex followed by carbonation is also observed on anorthite surface in our previous study.⁷⁵ HCO_3^- will eventually result in precipitation

Figure 5. Snapshot from *NVT* simulation of $10H_2O/4CO_2$ system, showing HCO_3^- formation (marked with a circle).

of geologically stable and environment-friendly mineral carbonates. ^{76,77}

We close by discussing the H₂O structure in these systems. In RDF of O–H for water in both 1W and 2W systems, there is a small peak around 1.8 Å, see Figure S4 in Supporting Information. This is a signature of hydrogen bonding among waters, indicative of water clustering in the system. This feature is evident in the presence of CO_2 , ⁵² however, in the presence of CH_4 in the system, it disappears at the higher hydration levels (8/10 H₂O, Figure S4).

3.2.2. Spectroscopic Properties. To provide spectroscopic signatures, we present the computed IR spectrum and *p*VDOS analysis to help identify the different species contribution to the IR spectrum, see Figures 6, S5, and S6. The frequencies below

Figure 6. IR spectrum (left panel) and pVDOS (right panel) with and without CO_2 intercalation. In *p*VDOS plot, color codes are given as follow: clay (red), H₂O (green), CH₄ (pink), and CO₂ (blue). For clarification, we doubled the intensities of H₂O, CH₄, and CO₂.

1000 cm⁻¹ are dominated by the Si–O–Si or Si–O–Al bending mode at 450 cm⁻¹, or the Si–O stretching mode at 950 cm⁻¹.^{52,78} The frequency range <1000 cm⁻¹ also includes contributions from the CO₂ bending mode (~600 cm⁻¹) and

water libration modes (\sim 700 cm⁻¹). The H₂O bending mode is shown as a weak peak at \sim 1600 cm⁻¹ and the frequencies between 3500 and 3750 cm⁻¹ include contributions from the free OH asymmetric and symmetric stretch bands of H₂O and clay. The broad feature between 3000 and 3500 cm⁻¹ corresponds to hydrogen bonding that becomes more pronounced in the presence of CO₂. Finally, the weak peaks between 1280 and 1500 cm⁻¹ correspond to HCH bending modes and the double peak at 3000–3200 cm⁻¹ correspond to CH symmetric and asymmetric stretching modes of methane.

Upon CO₂ intercalation, we observe a strong peak at ~2380 cm⁻¹ corresponding to CO₂ asymmetric stretch, while the two peaks in the range between 1200 and 1400 cm⁻¹ are the IR inactive Fermi dyad of scCO₂.⁷⁹ The 4H₂O/4CO₂, 8H₂O/4CO₂ systems also show two sharp peaks at ~1280 and 1720 cm⁻¹ which are similar to frequencies observed in IR spectrum of HCO₃^{-.80,81} To confirm this assignment, we deconvoluted the contributions from different CO₂ molecules in the 2W systems, Figure 6 and Figure S7 for all systems. While in the 4/6 H₂O systems all CO₂ molecules have similar contributions, in the 8/10 H₂O systems, the CO₂ found at ~2.5 Å from Ca, shows four distinguished peaks at ~780, ~ 920, ~ 1290, and ~1720 cm⁻¹, corroborating the bicarbonate formation.^{80,81}

In our previous paper,⁵² we have demonstrated that strong interactions between CO₂ and Ca²⁺ result in a blue shift of CO₂ asymmetric stretch band. A similar observation was also noted here, see parts a and b of both Figures 7 and S8. In the 4H₂O/ 4CO₂ system, the highest frequency C–O peak at ~2390 cm⁻¹ corresponds to the Ca-bound CO₂ (Ca–O_{CO2} at ~2.4 Å) while the lowest peak ~2361 (~2348 and ~2360) cm⁻¹ corresponds to CO₂ found at longer distances, ~ 4.3 Å. The 8H₂O/4CO₂ system shows similar behavior intermediate distances ~3.2 Å and a slightly lower blue-shift (~2377 cm⁻¹).

3.2.3. Molecular Dipole Moment and Intermolecular Interactions. Even though the average dipole moments of CO_2 and CH_4 over time are zero, as expected for apolar molecules, transient molecular distortions stimulate instantaneous dipole moments in these molecules. The instantaneous molecular dipole moments in CO_2 and CH_4 molecules can be computed by maximally localized Wannier functions (MLWF), as reported in previous studies.^{82–84} We followed the same approach using 1000 configurations extracted from our NVT simulations. Figures 7c and S8c show the histogram of dipole moments for each CO_2 molecule. In the 1W systems, it is clear that larger dipole moments are associated with strongly interacting Ca^{2+} and CO_2 , hence the blue shift in the

Figure 7. (a) pVDOS, (b) RDF of Ca $-O_{CO_2}$ and (c) histogram of dipole moment of each CO₂ molecule. Different color indicates different CO₂ molecules in a system and all figures use the same color codes. One of CO₂ dipole moments in $8H_2O:4CO_2$ system is excluded since it is converted to HCO_3^- corresponding to purple line in RDF plot. The gray dashed line in part a marks the asymmetric stretch (2363 cm⁻¹) in pure scCO₂.

asymmetric stretch envelope as discussed previously. Conversely, in the 2W systems no such strong $Ca^{2+}-CO_2$ interactions are present, resulting in smaller dipole moments for all the CO_2 molecules.

Figure 8 shows the histogram of the CH_4 dipole moments with maxima at ~0.4 D for all systems, except for $4H_2O$ that

Figure 8. Histogram of the molecular dipole moments of CH_4 for 1W (upper panel) and 2W (lower panel) systems.

shows an additional peak at 1.1 D. By deconvoluting the dipole moment of each CH₄, we find that the peaks at 1.1 and 0.4 D correspond to the first (~3.0 Å) and second (~5.5 Å) peaks in RDF of Ca $-C_{CH_4}$ (see Figure 4), respectively. We refer to these CH₄ molecules as Ca "Bound" or "Unbound" as indicated in Figure 9a. Since instantaneous dipole moments are due to

Figure 9. (a) Snapshot from *NVT* simulation, (b) distribution of bond length of C–H (solid lines) and C–Wannier centers (dotted lines) for unbound (red line) and bound (blue line) CH₄ to Ca²⁺, and (c) distribution of ∠HCH of unbound (upper panel) and bound (lower panel) CH₄ in 4H₂O. In part *c*, dotted line marks angle distribution of a gas phase CH₄ molecule, and orange arrows show motion of H for bound CH₄.

distortion of the CH₄ molecules, we calculated the distribution of C–H and C–Wannier center distances (Figure 9b), and the H–C–H and angles (Figure 9c), for both CH₄ molecules. Figure 9b shows that there is no distance difference between two CH₄ molecules. However, the angle distributions are markedly different between the Bound and Unbound CH₄ molecules, as shown in Figure 9(c). While the "Unbound" CH₄ shows an angle distribution centered at ~109.5°, the "Bound" CH₄ shows two distinct peaks at ~107.5° and ~111.0°. These larger HCH angles and further larger variations result in a CH₄ molecule that departs from the normal tetrahedral symmetry and as such it acquires a dipole. This counterintuitively large dipole moment of CH_4 is the result of strong interaction of Ca^{2+} cations with a normally apolar molecule, that is critical in understanding the adsorption/desorption mechanism and free-energetics relevant to methane recovery.

3.3. Adsorption Properties of CH₄ on the Ca–MMT Surface at 323 K. Adsorption isotherms were obtained by first estimating the adsorption free energies on external surface as a function of coverage (θ) using $\Delta G(\theta) = \Delta E(\theta) - T\Delta S(\theta)$. The adsorption energies (ΔE) were obtained from DFT calculations published previously,⁵⁶ and adsorption entropies (ΔS) were extracted from NIST isothermal data⁸⁵ at T = 323 K. The adsorption isotherm of CO₂ was also computed for comparison, see Figure 10. The obtained adsorption free

Figure 10. (a) Adsorption free energies (ΔG) of CH₄ and CO₂ as a function of coverage (θ). (b) Relative adsorption capacities of CH₄ and CO₂ as a function of partial pressure. Left: *y*-axis scales for theoretical estimates (th). Right: *y*-axis scales for experimental results (ex).

energies of CH₄ and CO₂ are shown in Figures 10a and S9, respectively. After accounting for the entropic contributions, ΔG becomes positive for $\theta > 0.3$ for CH₄, and 0.45 < $\theta < 0.8$ and $\theta > 1.2$ for CO₂. This means that for CH₄, a full monolayer is not likely, whereas for CO₂ a more complex phase behavior arises. For $\theta < 0.45$ both CH₄ and CO₂ can be coadsorbed, while for 0.45 < $\theta < 0.8$, an equilibrium between the CH₄ and CO₂ is prevalent. For $\theta > 0.8$, only CO₂ is expected to be found on the surface and for $\theta > 1.2$ CO₂ also starts desorbing. Note that our calculations find favorable energetics for a second layer of CO₂ (above $\theta = 1.0$) but not for CH₄. Given the coverage dependence of free energy, $\Delta G(\theta)$, an adsorption isotherm can be computed by solving the Langmuir isotherm as a function of CH₄/CO₂ pressure using the equation:

$$\theta = \frac{K(\theta)P}{1 + K(\theta)P}$$

where θ -dependent equilibrium constant is determined from $K(\theta) = \exp(-\Delta G(\theta)/k_{\rm B}T)$ with $k_{\rm B}$ being the Boltzmann constant. The amount of adsorbed CH₄/CO₂ is estimated from the obtained θ values and the mass of our clay model. Figure 10b shows estimated adsorption concentration as a function of

pressure along with experimental results.⁵⁶ We should note that in the absence of exact surface area measurements from experiment, the theoretical values cannot be directly compared to experimental one. However, the models are able to qualitatively reproduce the adsorption trends for both CH4 and CO2. While CH4 shows monolayer formation on Ca-MMT, CO₂ adsorption shows stepwise increase indicating that bilayers can be formed. For the first layer, adsorption concentration of CH_4 increases up to $P \approx 60$ bar (corresponding to $\theta \approx 0.3$) whereas that of CO₂ increases until *P* \approx 40 bar (corresponding to $\theta \approx 0.45$). As ΔG becomes positive, the coverage plateaus, see Figure 10a. In the case of CO_2 , a second layer starts forming at ~80 bar, corresponding to a minimum in ΔG . We also note here that a smooth increase of adsorption in the pressure range between 70 and 90 bar is observed during experiment with CO₂ indicating a mixture of mono- and bilayer formation at these pressures.⁵

By examining the local structure, we find that the most favorable sites for CH_4 adsorption are Ca^{2+} cation or surface OH sites. This can be connected to the induced dipole moments of CH_4 as discussed in the previous section. Calculation of the angle distribution in CH_4 shows the similar trends. Thus, we conclude that adsorption of CH_4 molecules on the clay surface is also strongly influenced by distortion of CH_4 molecule resulting in large dipole moment.

Finally, to interrogate the possibility of using CO_2 as a CH_4 carrier fluid, we performed a simulation with added CO_2 molecules above a CH_4 adlayer corresponding to maximum adsorption. The simulation showed that under these conditions, CO_2 replaces CH_4 on the surface within 20 ps; see Figure S10. This observation is consistent with our adsorption free energy calculations.

4. CONCLUSIONS

The current results demonstrate that a necessary ingredient for modeling methane-clay interactions is either AIMD, or a polarizable and flexible potential for methane in order to recover the abnormally large induced dipole moments in CH₄ considering its apolar nature. These dipoles are central to explaining the surface adsorption behavior and mobilization of adsorbed/intercalated methane. In the context of CO₂ monetization, methane recovery is possible using $scCO_2$ as an extraction fluid, not due to the affinity of CH₄ toward CO₂ as one might expect, but rather due to methane/water association in water-saturated $scCO_2$ fluids. Additionally, the higher CO_2 binding affinity for clay minerals, also facilitates the CH4 desorption. Investigation of competitive adsorption/desorption between scCO₂ and CH₄ on a Ca-MMT surface reveals that CH_4 adsorption increases up to a pressure ~60 bar, displaying favorable free energetics ($\Delta G < 0$). This allows the formation of stable CH_4 layer on the Ca–MMT surface. However, for P >60 bar, adsorption plateaus, and ΔG become positive. On the other hand, CO₂ has a lower adsorption free energy than CH₄ in the range between 0.8 and 1.2 coverage corresponding pressure range of \sim 70–90 bar where it preferentially adheres to the surface and further expels CH₄. For higher pressures (θ > 1.2) CO₂ adsorption becomes unfavorable ($\Delta G > 0$). Taken together, these results indicate that there is an optimal $scCO_2$ pressure window to maximize CH₄ extraction.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b05364.

(i) Binding energy between Ca²⁺ and molecule, (ii) optimized cell parameters and d-spacing for CH₄ intercalated Ca-MMT, (iii) optimized structure of $Ca^{2+}(H_2O)_6(CH_4)_2$ in $26CO_2$ simulation cell, (iv) distances between Ca²⁺ and neighboring molecules as a function of simulation time, (v) radial distribution functions (RDFs) for H₂O/CH₄/CO₂ on Ca-MMT, (vi) radial distribution functions (RDFs) and its integral for $Ca^{2+}(H_2O)_n(CH_4)_{2}$, (vii) IR spectrum and pVDOS of 1W systems, (viii) IR spectrum and pVDOS of 2W systems, (ix) pVDOS of each CO_2 in the CO_2 intercalated systems and temperature dependence of the VDOS, (x) pVDOS, RDF of Ca-O_{CO}, and histogram of dipole moment for each CO₂ molecule, (xi) adsorption free energetics of CH_4 and CO_2 on Ca-MMT, and (xii) snapshot of NVT simulations at 0 and 25 ps for 26 CO₂ above CH₄ adlayer on Ca-MMT (PDF)

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Notes

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