Adsorption of water and CO_2 on calcite and clathrate hydrate: the effect of short-range forces and temperature

Phan Van Cuong, Bjørn Kvamme, Tatiana Kuznetsova*, Bjørnar Jensen

Abstract—The promising technique of carbon sequestration in geological formations can contribute both to greenhouse effect reduction and enhanced oil recovery. Given that all processes occurring during injection, post-injection, and storage occur in the porous rock matrix, the interactions and reactions between CO_2, water, and minerals will be of utmost importance and must be carefully considered. We applied molecular dynamics (MD) simulations to study interfacial systems that included both aqueous, carbon dioxide, and mineral surfaces with the focus on the impact of force field, calcite and temperature variations. Our investigation showed that CO_2 transport and interface stability were substantially affected by temperature, calcite, and force field utilized. As temperature increased, the number of CO_2 molecule crossing water layer and adsorbing on calcite surface increased while adsorption stability deteriorated. When we applied Buckingham potential between water and calcite, all other interactions were Lennard-Jones (L-J), electrostatic contribution proved to be the deciding factor with the coordination of CO_2 oxygen towards the calcium ions in calcite being the most important factor that ensures the stability of calcium-CO_2 pairs. When Buckingham potential is applied for both water-calcite and CO_2-calcite interactions, with the rest being L-J in form, the CO_2 coordination towards the carbonate becomes the dominant orientation instead.

Keywords—Adsorption, Calcite, Carbon Dioxide, Molecular Simulation.

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I. INTRODUCTION

CARBON dioxide can be captured, transported, and permanently stored in geological formations including spent petroleum reservoirs [1], [2]. This promising technique of carbon sequestration can contribute both to greenhouse effect reduction and enhanced oil recovery (EOR). However, all processes occurring during injection, post-injection, and storage occur in either porous rock or inside rust-covered pipes, making interactions and reactions between CO_2, water, and minerals to be of utmost importance.

Calcite is one of the most abundant minerals in the Earth's crust, with $(10\bar{1}4)$ plane being the most stable [3] and by far the dominant observed morphology of calcite in situ [4]. Atomistic-scale interactions between $(10\bar{1}4)$ calcite surface and various substances like pure water, aqueous solutions, peptides, etc. have been the subject of several numerical studies already [5]-[10]; it continue to draw interest because of the decisive role they play in determining both macroscopic properties and kinetics of processes.

There were two main reasons that led us to use the conventional approach shared by a number of other researchers [5]-[10] by disregarding the reactions between water and carbon dioxide. The first one has to do with the size limitations of even reasonably large numeric simulations. According to our simple calculations, including even a few unbalanced hydronium ions to mimic the effect of the pH would require the presence of at least half a million of water molecules. Such a simulation is currently not feasible.

A good example of the size necessary to reflect the realistic concentration can be provided by considering the conditions at the Utsira formation, which is longest-running injection site of carbon dioxide storage [2], [11]. The pH at Utsira ranges around 3, with temperature and pressure being 5° C and 50 atm, respectively. Estimates that employed the geochemical package from ATHENA [9], [11] have shown that CO_2 dissolved in water at those conditions will be dominated by

molecular CO_2. One would need to introduce about 275 CO_2 molecules per bicarbonate ion, in case of our system, it would mean increasing the number of water molecules by more than the factor of 30. In view of this, it was decided at this stage not to include any dissociated product of CO_2 in water solution but potentially at a later stage investigate the impact of bicarbonate and hydronium together with CO_2 on the adsorption characteristics and reactions.

The other important aspect that made us reluctant to consider the reactions is linked to the nearby presence of two other phases, the carbon dioxide liquid and the calcite surface. Carbon dioxide readily diffusing from the carbon dioxide phase will undoubtedly skew the reactions, making it difficult to apply the results of bulk calculations. In the recent van Duin paper [12] that utilized the sophisticated reactive force field (ReaxFF) [13] approach allowing one to include the possible reactions between the components in the course of molecular dynamic simulations, it was shown that bicarbonate formed from water and CO_2 will try to escape the water cluster environment and move to the outside within the time span of their MD simulation.

For our system, it would mean that any newly formed ions would rapidly migrate to calcite interface and adsorb onto it. As such the water/CO_2 interface would still be out of dissociation equilibrium. The absence of reliable experimental data capable of resolving the question of how the calcite surface will be modified in the presence of reactions between water and CO_2 made us believe that attempts to include the reactions are more likely to incur errors rather than bring any additional insight into the system under study.

In this work, we used molecular dynamics simulations to study several aqueous interfacial systems involving CO_2 and calcite. Our main focus was to investigate the impact of calcite and temperature variations on transport, adsorption, and stability of CO_2 molecules and water as affected by the presence of $(10\overline{1}4)$ calcite surface. A special attention was paid to role of short-range contributions to the intermolecular potentials.

II. SYSTEM SETUP AND MOLECULAR SIMULATION DETAILS

The composite system was built from a 1620-atom slice of calcite crystal [14], [15], two water slabs, a hydrate crystal, and a carbon dioxide phase with the density corresponding to 200 atm and 277 K. The calcite slice was positioned in the middle of the 40 Å-thick liquid water block and parallel to the initial water-CO_2 interface. A carbon dioxide hydrate slab composed of 4x4x2.5 structure I unit cells was added to probe the potential competition for carbon dioxide between hydrate and calcite in reservoirs under conditions where hydrate formation is possible. The second water phase consisted only of 500 water molecules meant to cushion the hydrate crystal from the carbon dioxide. The resulting primary simulation cell ranged 48 x 48 x 108 Å in size and is shown in Fig. 1.
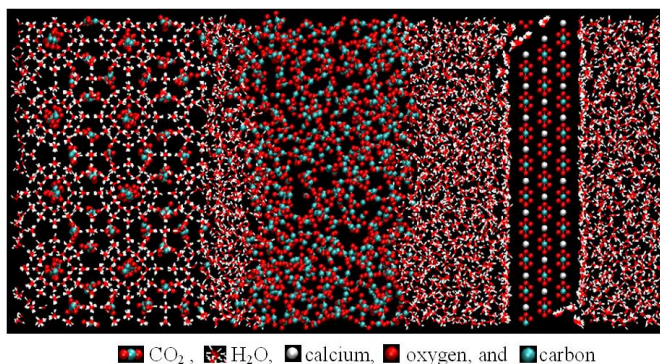

CO$_2$,   H$_2$O,   calcium,   oxygen, and   carbon

Fig 1. Side view snapshot of the initial system.

A. Fractional charges in calcite

Maestro/Jaguar quantum chemistry package [16], [17] utilizing B3LYP with [PS] LACVP basis set and with force convergence flag set was used to estimate the partial charges in vacuum for a 210-atom calcite slab cleaved along the dominant $(10\overline{1}4)$ plane. Except for the edges of the crystal, vacuum charges proved to be quite uniform. These values are listed in Table I; they agree quite well with those of Fisler, *et al.* [18] where the calcium ion charge were kept fixed at +2, and the focus was on the carbonate group, allowing carbon and oxygen charges to vary but constraining their sum to -2. In our approach that used Maestro/Jaguar, all atomic charges in calcite were free to vary while their sum was constrained to zero. The charges were then mapped onto a 1620-atom calcite slab cleaved out of a larger calcite crystal along the $(10\overline{1}4)$ plane.

Table I. Fractional atomic charge in calcite

Atom	Fractional charge (e)	
	This work	Fisler, *et al.* [18]
Calcium	1.881	2.000
Carbon	1.482	1.344
Oxygen	-1.118	-1.115

B. MD details

Molecular dynamics MDynaMix package [19] was employed, with temperature kept constant at three different temperatures (277, 388, and 500 K). The time step was 0.5 fs, with periodic boundary conditions applied in all three directions. The cut-off radius for the Lennard-Jones potential was set to 10 Å.

Our molecular dynamics used the rigid body treatment for all molecules. All calcite crystal atoms were fixed in place, as our previous studies found the rearrangement of hydrate calcite surface to be rather small. Water molecules in hydrate were locked in space but free to rotate around their centers,

while the CO_2 guests were completely free. We used Linux-based Message-Passing Interface (MPI) to run the MD simulations in parallel on 88 processors of Cray XT4 supercomputing facility at the University of Bergen, Norway.

Force fields and the impact of short-range interactions

The force field used the conventional approach describing potential energy as a sum of individual non-bonded energy terms with two contributions, the electrostatics and the van der Waals. Conventional Lorentz-Berthelot mixing rules were used to calculate the cross interactions. The short-range potential energy between CO_2 and water was represented by the Lennard-Jones potential of [20] and modified F3C [21], [6] models, respectively.

The inclusion of carbon dioxide in the system resulted in the additional challenge concerning the description of interaction between calcite and CO_2.

In the absence of available experimental results characterizing the behavior of carbon dioxide close to calcite or similar minerals, we found it necessary to test a series of short-range potentials that ranged from pure Lennard-Jones, a combination of Lennard-Jones and Buckingham potentials, and pure Buckingham interactions between calcite and CO_2, with the Buckingham CO_2 model fitted to reproduce bulk properties [22] (see Table II). The functional form of the Buckingham potential used is presented in (1), with the arithmetic rules of (2) applied to calculate the cross-interaction parameters:

$$U_{ij}^B = -\frac{C_{ij}}{r_{ij}^6} + A_{ij}e^{-\frac{r_{ij}}{\rho_{ij}}} \qquad (1)$$

$$A_{ij} = \sqrt{A_{ii} * A_{jj}} \qquad (2)$$

The Lennard-Jones parameters used for calcite were taken from [23] which featured a rather deep and narrow well in case of the calcium ion. The goal of this unusual force field was apparently to emphasize the role of short-range contributions to override the normally dominant electrostatic forces [5], [24], [25].

Table II. Lennard-Jones and Buckingham force field parameters for carbon dioxide ([20], [22]) and water ([3], [21])

	C	O in CO_2	O in H_2O	H in H_2O
Charge (e)	0.6512	-0.3256	-0.8476	0.4238
σ (Å)	2.7570	3.0330	3.1666	0.8021
ε (kJ/mol)	0.2339	0.6657	0.7732	0.04184
C (kJ $Å^6$/mol)	1491.6	1629.9	2889.7	106.2
A(kJ/mol)	909.23	1483300.0	293206.3	11537.16
1/ ρ (1/Å)	2.27	4.4	3.659	3.875

Table III. Lennard-Jones and Buckingham force field parameters for calcite

	Ca^{+2}	C	O
Charge, q (e)	1.881	1.482	-1.118
σ (Å)	0.899	3.742	2.851
ε (kJ/mol)	113.819	0.5021	0.6657
C (kJ $Å^6$/mol)	55686.7	2432.71	1123.56
A (kJ/mol)	82942.86	369822.7	230230.1
1/ρ (1/Å)	2.198	3.6019	3.9602

Table IV. Location and depth of minima for Buckingham interaction between calcite and CO_2

Calcite-CO_2	r_{min} (Å)	Depth (kJ/mol)
C (calcite) - C (CO_2)	3.80	-0.282
C (calcite) - O (CO_2)	3.67	-0.480
Ca (calcite) - C (CO_2)	N/A	N/A
Ca (calcite) - O (CO_2)	4.15	-0.994
O (calcite) - C (CO_2)	3.50	-0.303
O(calcite) - O (CO_2)	3.44	-0.477

Table V. Location and depth of minima for Buckingham interaction between calcite and water

Calcite-H_2O	r_{min} (Å)	Depth (kJ/mol)
C (calcite) - H (H_2O)	3.54	-0.140
C (calcite) - O (H_2O)	3.73	-0.551
Ca (calcite) - H (H_2O)	3.87	-0.339
Ca (calcite) - O (H_2O)	4.11	-1.280
O (calcite) - H (H_2O)	3.31	-0.142
O (calcite) - O (H_2O)	3.48	-0.556

As seen from Table II, the Lennard-Jones radii and well depths of water and carbon dioxide oxygen are not too dissimilar, which would make the short-range interactions of water and carbon dioxide with calcite comparable in strength. In this case one would expect the electrostatics to determine the relative affinities between various substances and the mineral surfaces.

The Buckingham potential between calcite and water was adapted from [3]. The comparison of Buckingham interactions between the different sites of water and carbon dioxide required a graphical treatment summarized in Tables IV and V. As in case of the Lennard-Jones potential, locations and depths of the cross interaction are quite similar for water and CO_2. Both calcium and carbon in carbon dioxide bear significant positive charges, making the purely attractive nature of their short-range interaction non-problematic, as proven by simulations.

III. RESULTS AND DISCUSSION

A. "Hybrid" Lennard-Jones -- Buckingham system

This system was characterized by the unusually strong Lennard-Jones interaction between calcium in calcite and carbon dioxide [23] and regular Buckingham potential for water and calcite [3].

At all three temperatures (277, 388, and 500 K), CO_2 molecules managed to cross the aqueous layer to reach the calcite slab surface where they were able to successfully displace the original water molecules from the vicinity of calcium ions. The simulation results have also showed that CO_2 transport and adsorption stability were heavily affected by the presence of calcite and temperature variation. For example, the simulations of [23], which utilized a similar system setup and combination of force fields but included a calcite nano-crystal instead of a large surface, found that no CO_2 molecules were able to come closer than 6 Å to the crystal at all temperatures. Those findings are in stark contrast with this work and point to the possible importance of collective effects.

Fig. 2c shows the number of adsorbed CO_2 molecule on $(10\bar{1}4)$ calcite surface as a function of simulation time. At the lowest temperature (277 K), water-CO_2 interface of MD simulation system was relatively non-volatile. The number of CO_2 molecules that successfully crossed the water layer and adsorbed onto the $(10\bar{1}4)$ calcite surface was enough to cover only a fraction of the calcite surface during 7.5 ns of the simulation time. At a higher temperature (388 K), CO_2 molecules had enough kinetic energy to easily cross the water layer and adsorb on the calcite surface, with the water-CO_2 interface mostly retaining its original flat shape. This was in stark contrast with the situation at 500 K, where the water-CO_2 interface was highly volatile with vigorous intermixing of water and CO_2. A large number of CO_2 molecules crossed the aqueous layer and were adsorbed onto $(10\bar{1}4)$ calcite surface.

When CO_2 molecules approached the calcite surface, they tended to coordinate to the calcium ion so as to maximize the electrostatic attraction by pointing one of their oxygen atoms towards the calcium ion, as shown in Fig. 2 (a- side view, b-top view). The adsorption process appeared to reach saturation at 500 K when each calcium ion of $(10\bar{1}4)$ calcite surface had

adsorbed a CO_2 molecule. When two CO_2 molecules were competing for the same calcium, only one achieves the energetically favorable position, while the other either left the surface and re-entered the water bulk or found another calcium ion.
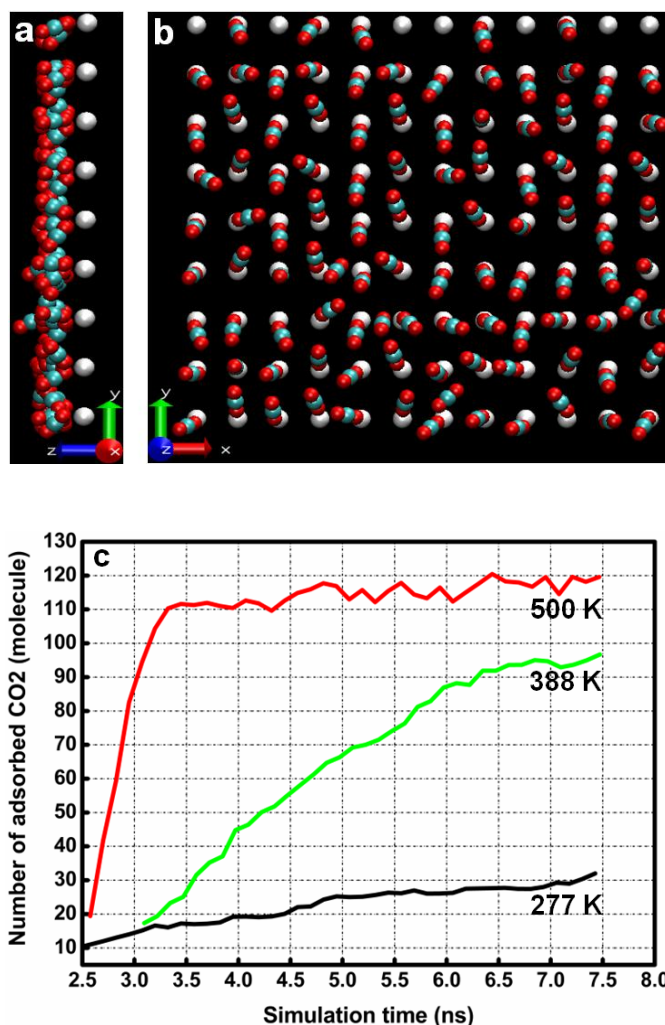

Fig. 2. Side view (a) and top view (b) snapshots of the $(10\bar{1}4)$ calcite surface at 500 K after 7.5 ns. One CO_2 molecule adsorbed by calcium ion. (c) shows the number of adsorbed CO_2 molecule as a function of simulation time. (Calcium: white; Oxygen: red; Carbon: cyan)

The demonstrated affinity of carbon dioxide for the calcite surface and its ability to displace the previously adsorbed water molecules was quantified further by comparing the energies of water and CO_2 in different environments. We have used Visual Molecular Dynamics (VMD) [26] with NAMD Energy Plugin version 1.3 [27] to estimate energies characteristic for $(10\bar{1}4)$ calcite surface and adsorbed CO_2 molecules, and water molecules adsorbed on the other side of calcite where they did not have to compete with carbon dioxide. The energies were obtained by summing all non-bonded interactions between water and CO_2 molecules within 5 Å of calcite. These values were heavily dominated by

electrostatic contributions, making the error of using the Lennard-Jones instead of Buckingham potential for water rather negligible.

The adsorption energy per molecule between $(10\overline{1}4)$ calcite surface and bulk H_2O or adsorbed CO_2 molecules is plotted in Fig. 3 for all three temperatures. The values are average over 500 trajectory frames obtained after 7.5 ns of simulation. As seen from the figure, the adsorption energy of water was significantly higher than that of carbon dioxide at all three temperatures, indicating the preference for carbon dioxide over water on calcite surface, and explaining why water molecules were replaced by the CO_2.

The adsorption energy of CO_2 molecules also appeared to become smaller with increasing temperature, accounting for the somewhat lower stability and subsequent number fluctuations of adsorbed carbon dioxide at 500 K (-75.5 kJ/mol at 277 K versus -63.6 kJ/mol at 500 K). The adsorption energy amounted to -71.1 kJ/mol at 388 K, falling in between 277 K and 500 K. We have also run separate MD simulations to estimate the energies of CO_2 in bulk (same density and temperature as the CO_2 slab used in the composite system) and dissolved in water at 2.9 mole fraction. The potential energy amounted to $-10.16(6)\pm2$ kJ/mol and $-25.(5)\pm5$ kJ/mol, respectively, proving to be significantly smaller than the adsorption energy. Even when one takes into consideration significant motion constraints imposed on adsorbed molecules, especially at surface saturation, the incurred entropy penalty will be more than offset by the energetic benefits of adsorption on calcite.
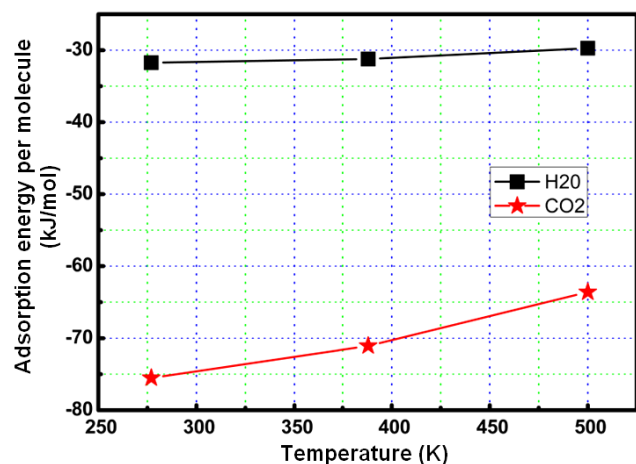

Fig. 3. Average adsorption energy per molecule after 7.5 ns of simulation

B. *Pure Lennard-Jones interaction with calcite*

When purely Lennard-Jones force fields were used for water and carbon dioxide interaction with calcite, it was water that completely dominated the adsorption on calcite, preventing carbon dioxide from adsorbing. We have applied the Lennard-Jones interaction after running the initial system for a period sufficient for 2 carbon dioxide molecules to be firmly adsorbed onto the surface at 277 K. When the switch was made to the Lennard-Jones interaction between water and calcite, one of the molecules immediately left the surface, while the other remained stuck to the surface, with no new CO_2 able to approach the surface during 4.1 ns of the simulation time.

C. *Pure Buckingham interaction with calcite*

We used the same initial configuration as in the previous section to switch the system to purely Buckingham force field for calcite interaction with water and carbon dioxide. In contrast to the case of pure Lennard-Jones interactions, both carbon dioxide molecules initially left the surface at the lower temperatures (277 K and 388 K). As proven by identical pair correlation functions between water and calcite atoms (Figs. 4 and 5), the pattern of water adsorption remained identical on the both sides of the calcite sliver, being apparently unaffected by the presence of hydrate and carbon dioxide layers. The RDFs show that the alignment of water towards calcite was mostly decided by electrostatics, with the oxygen and hydrogen tightly coordinated to the oppositely charged ions, calcium for oxygen and oxygen for hydrogen.
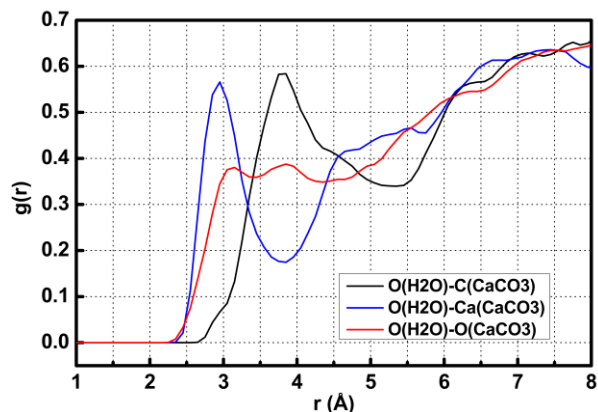

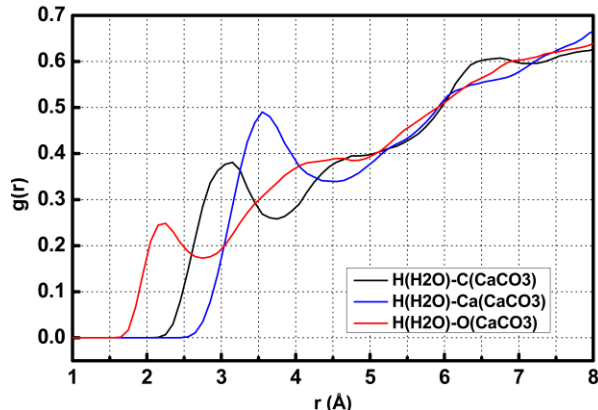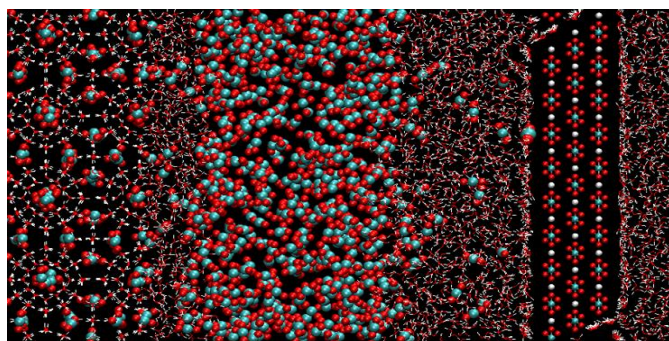Fig 4. Radial distribution function for oxygen in water adsorbed on calcite at 277 K.

Fig 5. Radial distribution function for hydrogen in water adsorbed on calcite at 277 K.

The subsequent simulations showed that while water continued to heavily dominate the adsorption on calcite, several CO_2 molecules managed to come into contact with the surface and even adsorb for a fraction of the run at the lower temperatures. The final alignment of adsorbed CO_2 molecules at these temperatures was entirely different from the Lennard-Jones case. As seen in the snapshot of Fig. 6 and indicated by the radial distribution functions plotted in Fig. 7, the carbon dioxide molecules are now seeking to maximize the electrostatic attraction by positioning itself flat on the surface and coordinating towards the carbonate ion instead of calcium.

CO_2 ■■, H_2O ▨, and Calcite (Ca ▢, C ▨, O ▮)

Fig 6. Side view of the Buckingham system at 277 K after 1.08 ns of simulation. Note the drastically changed alignment of adsorbed CO_2 molecule.
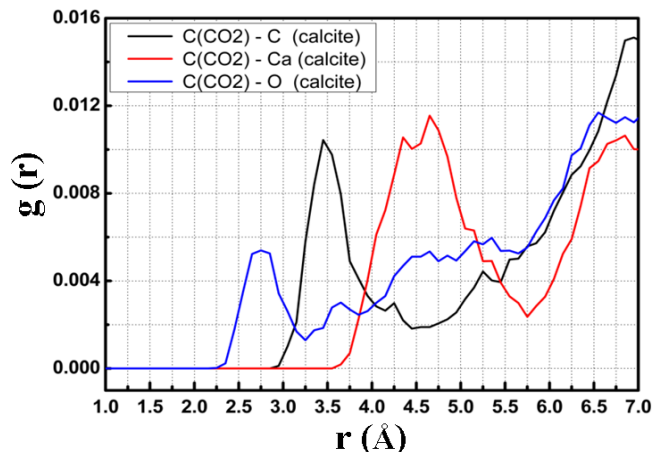

Fig 7. Radial distribution function for carbon in dioxide molecule adsorbed on calcite at 277 K.

As seen in Fig. 7, the closest distance between carbon in carbon dioxide and calcium in calcite is around 4.5 Å; this separation corresponds to an almost-zero Buckingham pair-wise energy, eliminating any danger of unphysical sorption. The CO_2 molecule remained attached to the same adsorption spot for several hundreds of picoseconds. The preferred orientation in terms of the angle between adsorbed CO_2 and the xy-plane is plotted in Fig. 8.
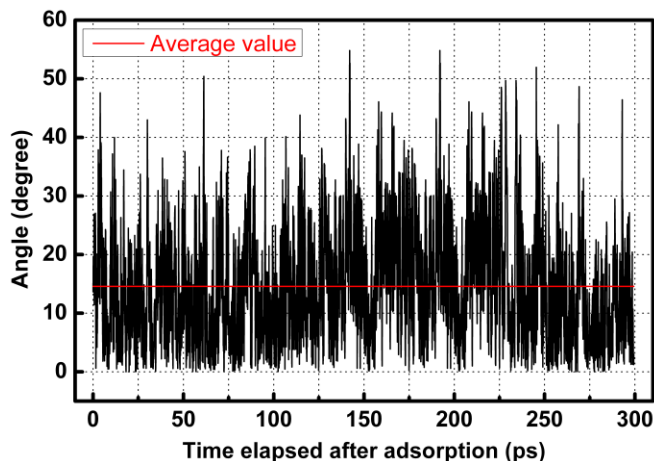

Fig. 8. Purely Buckingham system at 277 K, 3.7 ns after the switch. Angle between adsorbed CO_2 and the xy-plane. Average angle: $14° \pm 10°$.

The adsorption of carbon dioxide was somewhat higher at the temperature of 500 K. This higher adsorption rate was due to the vigorous intermixing of the carbon dioxide and water at this temperature that virtually destroyed the interface. As shown in Fig. 9, a number of CO_2 molecules could be found in the immediate vicinity of the calcite surface at any point in the simulation, with several of them adsorbing onto the surface itself.
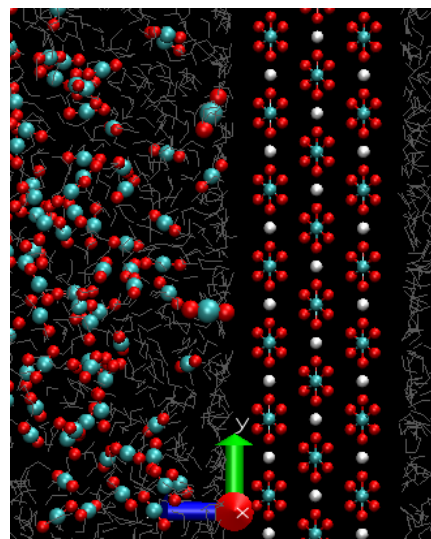

Fig 9. Purely Buckingham system at 500 K, 3.6 ns after the switch. Note the significantly larger number of carbon dioxide molecules at the calcite surface (Calcium: white; Oxygen: red; Carbon: cyan; Water: gray)

In contrast to the behavior exhibited by adsorbed carbon dioxide in the other studied systems, the stability of adsorption at 500 K was much lower. The carbon dioxide molecules was shown to easily leave the surface for the bulk to be replaced by other carbon dioxide molecules, as well as move along the surface from one adsorption site to another. The snapshot in Fig. 10 presents a typical picture of the two preferred

orientations that could be assumed by carbon dioxide molecules close to the calcite mineral surface, one with carbon dioxide oxygen normal to the surface and coordinated against calcium (as seen in RDFs of Fig. 11), and the other identical to the one at 277 K, *i.e.* the molecule lies flat against the surface close to the carbonate ion and with RDFs very similar to those in Fig. 5.
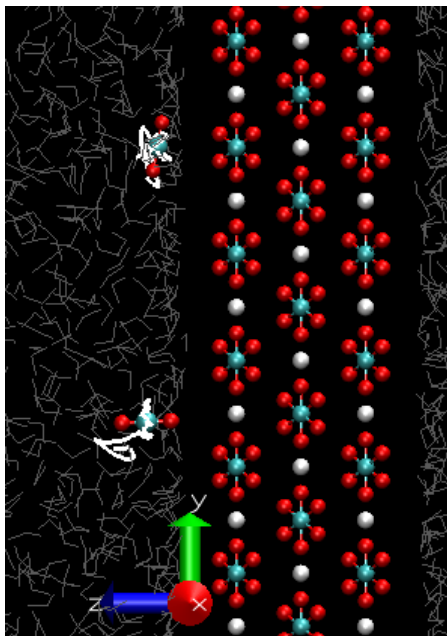

Fig 10. Purely Buckingham system at 500 K, 3.6 ns after the switch. Both white lines show trajectories followed by the molecules over 5 ps while the lower one remained adsorbed. (Calcium: white; Oxygen: red; Carbon: cyan; Water: gray)
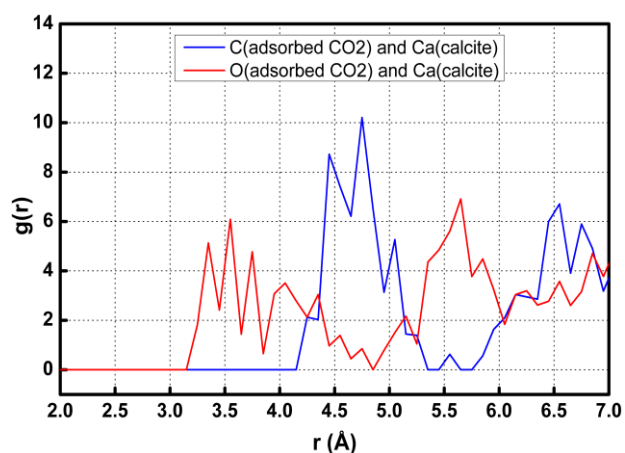

Fig 11. Radial distribution function for oxygen in dioxide molecule adsorbed on calcite at 500 K and coordinated to calcium cation

These orientations were quantified in terms of the angle between adsorbed CO_2 and the *xy*-plane; they are plotted in Fig. 12. The analysis of trajectories characteristic of the two preferred alignments showed that the planar orientation was significantly more stable than the orthogonal one. Carbon dioxide molecules coordinated to the carbonate remained

attached for 15 to 50 ps before leaving the surface and being replaced by other CO_2 molecule; while the molecules attached to the calcium ion usually stayed at this position for only few picoseconds at a time as indicated in Fig. 12 by the abrupt ending of the red line and by uneven RDF curves in Fig. 11.
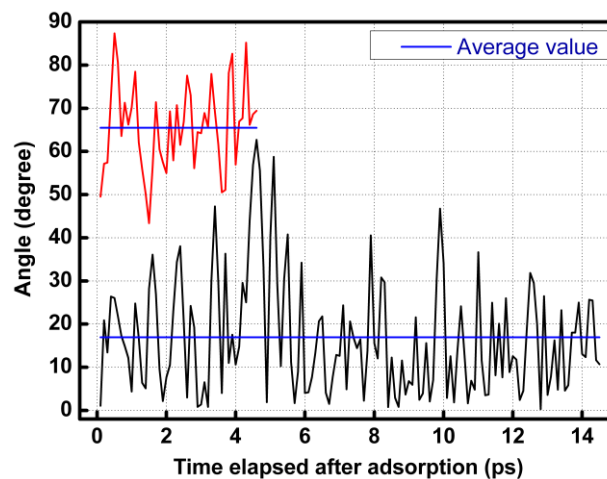

Fig 12 Angle between adsorbed CO_2 and the *xy*-plane Purely Buckingham system at 500 K, 3.6 ns after the switch. Black line: planar orientation, average angle 17˚±13˚. Red line: orthogonal alignment, average angle 66˚±10˚.

The adsorption energy per molecule between $(10\bar{1}4)$ calcite surface and bulk H_2O or adsorbed CO_2 molecules is plotted in Fig. 13 for all three temperatures. The values are averages over 500 trajectory frames obtained after 1.08 ns of simulation. The figure shows that the adsorption energy of carbon dioxide was higher than that of water at all three temperatures, with the largest difference equal to 11 kJ/mol at 388 K. Although the calcite surface showed clear preference for water over carbon dioxide, as shown in Fig. 6 and Fig. 8, CO_2 managed to adsorb onto calcite, with the stable adsorption of 1 molecule attached to the surface throughout the simulation even at temperatures characterized by a stable water-carbon dioxide interface.

This finding was in contrast to the total inability of carbon dioxide to even approach calcite in case of a nano-crystal [23]. This difference can be explained by the effect of the large surface that encouraged several CO_2 molecules at once to compete with water molecules, allowing some of them to successfully attach to calcite. At the highest temperature (500 K), CO_2 molecules will have the largest kinetic energy, thus many CO_2 molecules were able to reach the calcite surface quickly. The high kinetic energy also made it easy leave or move along the calcite surface. Fig. 14 shows the typical behavior of a CO_2 molecule close to the calcite surface during an interval of 50 ps: small "vibrations" while being coordinated to one carbonate anion followed by leaving the surface but remaining in the next water layer, and re-adsorbing onto a different carbonate in the same planar orientation.
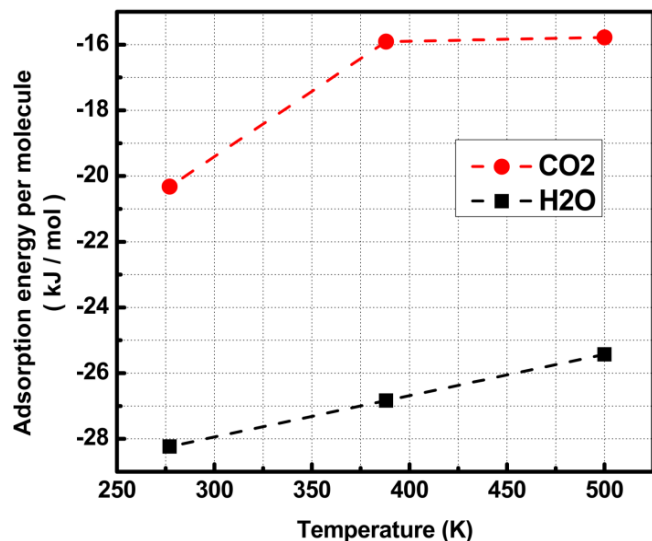
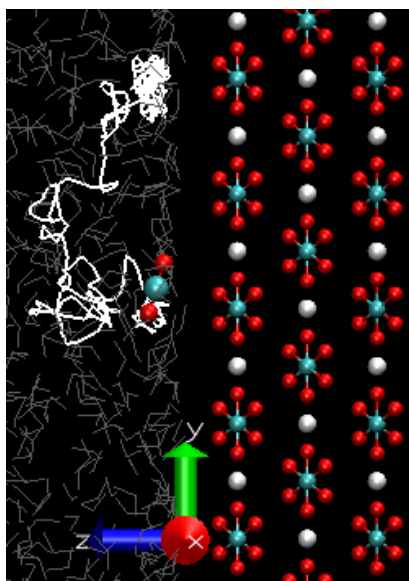Fig. 13 Average adsorption energy per molecule after 1.08 ns of simulation

Fig. 14 White line: a typical trajectory of an adsorbed CO_2 at 500 K, 3.6 ns after the switch. (Calcium: white; Oxygen: red; Carbon: cyan; Water: gray)

IV. CONCLUSION

Our investigation showed that CO_2 transport and interface stability were heavily affected by temperature, calcite, and force field utilized. As temperature increased, the number of CO_2 molecule crossing water layer and adsorbing on calcite surface increased while adsorption stability deteriorated for all the investigated combinations of short-range potentials.

When we applied Buckingham potential between water and calcite, with all the other interactions being Lennard-Jones, the electrostatic contribution proved to be the deciding factor with the coordination of CO_2 oxygen towards the calcium ions in calcite being the most important factor that ensured the stability of calcium-CO_2 pairs. When Buckingham potential is applied for both water-calcite and CO_2-calcite interactions, with the rest being Lennard-Jones in form, the coordination of CO_2 carbon towards the carbonate oxygen becomes the decisive factor. Our investigation has also highlighted the crucial importance of reliable force fields suitable for describing the interactions between carbon dioxide and calcite. While the decidedly more physical and intuitive behavior displayed by purely Buckingham interactions between water, carbon dioxide, and calcite makes this combination a clear favorite, the best way to parameterize the CO_2-calcite interaction potential would through be fitting its parameters against experimental data for carbon dioxide.

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