Diffusion of gas mixtures in the sl hydrate structure

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The exchange of methane with carbon dioxide in gas hydrates at the deep ocean has been suggested as a manner harvest methane while at the same time store carbon dioxide. Experimental evidence suggest that this process is facilitated if gas mixtures are used instead of pure carbon dioxide. We studied the free energy barriers for diffusion of methane, carbon dioxide, nitrogen, and hydrogen in the sI hydrate structure using molecular simulation techniques. Cage hops between neighboring cages were considered with and without a water vacancy and with a potential inclusion of an additional gas molecule in either the initial or final cage. Our results give little evidence for enhanced methane and carbon dioxide diffusion if nitrogen is present as well. However, the inclusion of hydrogen seem to have a substantial effect as it diffuses rapidly, can easily enter occupied cages, while reducing the barriers for the gas molecules that co-occupy a cage with hydrogen.

I. INTRODUCTION

As a stopgap measure, it can be desirable to replace coal with cleaner fossil fuels, such as methane. To this purpose, harvesting methane from the vast[1] hydrate reservoirs at the sea floor and in permafrost regions has garnered significant amounts of attention[2–9]. When in contact with methane at high pressures, water forms the sI clathrate structure, trapping methane molecules in cages. The unit cell of the sI clathrate structure is formed by 46 water molecules. The water molecules are arranged in rings that define two types of cages, shown in figure 1.
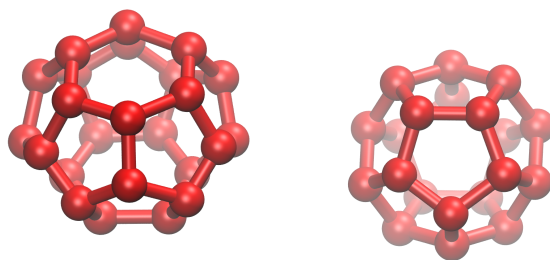

FIG. 1 The large (left) and small (right) cages that combine in a 6-2 ratio to form the unit cell of the sI hydrate. Only oxygen atoms are visualized for clarity.

The small cage is a regular dodecahedron with 12 5-membered water rings, while the large cage, consists of 12 5-membered rings and 2 6-membered rings. In one unit cell, there are 2 small and 6 large cages. Due to their orientation in the large cage, diffusion through the 6-membered rings can only facilitate a one-dimensional diffusion process[10]. To diffuse to any generic point, the guests must at some point jump through 5-membered rings. The small cages are only connected to large cages. The occupancy of the cages varies with pressure and guest type. For methane at 100 bar, simulations[11,12] predict that the large cages are $\sim 97\%$ occupied, while the small cages are $\sim 87\%$ occupied.

The simplest method of harvesting methane from those hydrates is by destabilizing the hydrates. This can be done either by heating the hydrates, or by depressurizing them. These two methods are straightforward, but they necessitate the destruction of the hydrate crystal structure. The destruction of the hydrate structure can destabilize the hydrate reservoir, mostly encapsulated

in sandstone, resulting in an excessive release of water from the layer below the hydrate-rich zone[8,9]. This release of water is also associated with uncontrolled production of sand[8,9], which can halt harvesting operations.

To avoid these issues, a harvesting method in which methane is replaced by carbon dioxide is actively researched[2–6]. In this case, the hydrate would maintain its structure, keeping the reservoir intact. Additionally, this could serve as a storage of carbon dioxide, and the exchange fulfills two purposes at once. As it is cheaper to procure, it is desirable to use a mixture of carbon dioxide and nitrogen, rather than pure carbon dioxide[2]. In practice, using a mixture of nitrogen and carbon dioxide also appears to increase the amount of methane recovered relative to pure carbon dioxide[2–4]. It should be noted that as the percentage of nitrogen increases, the stability of the resultant is reduced, as mixed CO_2/N_2 hydrates have a lower melting temperature than pure CO_2 hydrates. As such, one would also expect the driving force associated with harvesting CH_4 to be reduced with increasing percentages of N_2. The fact that mixtures still seem to result in improved rates of methane recovery, is frequently explained as nitrogen being better at occupying small cages than carbon dioxide[2].

The exchange process can be divided into two parts[2,13,14]. The first part is the initial exchange at the surface of the hydrate, which occurs by a partial dissolution of the methane hydrate into the replacement fluid followed by an immediate enclathration of the surrounding fluid. Due to the barriers involved, this process is assumed to occur at a hight rate than simple penetration of gas molecules through the windows lying at the surface of the hydrate. The second part is the exchange that occurs in the bulk of the hydrate, where there are two possible mechanisms to consider for the exchange of methane with carbon dioxide. The exchange can happen by a progression of microscopic scale dissociations of methane hydrate, leading to a partially decomposed hydrate. This is then rapidly followed by a formation of carbon dioxide hydrate[2]. For this mechanism to allow for an exchange in the core of the hydrate, mass flow of methane and carbon dioxide must necessarily occur along channels that are outside the hydrate system. These channels could be fault lines between crystal grains, or the edges of nanoporous materials where the hydrates are formed. If such channels of mass transport are not present, the exchange can only occur on the surface of the hydrates. The second potential description of the exchange mechanism relies on the cage-to-cage diffusion of guest molecules, according to the "hole in the cage wall" principle[10,15].

According to this line of thought, a guest molecule can hop from one cage to a neighboring empty cage, provided that a water molecule is missing from the ring of water molecules that define the interface between the two cages. With no vacancies present, the trapped gases have to overcome significant free energy barriers in order to hop between cages. This description is known to provide a good explanation for the conversion of ice to gas hydrates[16–18] when exposed to high pressured gases. Additionally, it appears to provide a sensible explanation for exchange experiments[13].

The diffusion of guest molecules in the bulk of the hydrate is slow, especially for methane[10,19]. For gas-exchange to be a viable approach to harvesting methane hydrates, it would be helpful to properly understand the process driving the diffusion, and whether it can be sped up. The molecular simulations studying the diffusion of guest molecules in the bulk of gas hydrates have to this date focused on hydrates formed by single guest components, such as pure CH_4 hydrates[10] or pure CO_2 hydrates[15,19]. While brute force MD-simulations have shown signs of (short-lived) multiple occupation of cages[19], studies using advanced sampling techniques[10,15] have only considered cases where guests hop from singly occupied cages to empty cages, assuming that it is safe to ignore temporary double occupancy of cages. For pure hydrates, this assumption is reasonable - the most likely event after a cage is multiply occupied, is a molecule of the same type hopping back into the emptied cage. For hydrates with multiple types of guests, this is not necessarily the case. If the multiply occupied cage is sufficiently metastable, it is possible for the guest molecules to trade places, without requiring hops into empty cages as intermediate steps.

Ding et al.[6] performed experiments using a mixture of hydrogen and carbon dioxide as the replacement gas, and found that this mixture had a higher rate of methane recovery than pure carbon dioxide, without consuming the hydrogen gas. They propose that hydrogen could act as a promoter of the exchange, "attacking" the methane that is stuck in cages, and allowing the exchange to occur more rapidly. It is known that hydrogen moves with relative ease within sII-hydrates[20–22]. Molecular simulations[21,22] show that the multiple occupancy of cages helps reduce the free energy barrier for hydrogen hopping between cages. It is possible that a similar effect can occur when hydrogen gas is present in the exchange between methane and carbon dioxide - even if it is clear that hydrogen does not remain enclathrated in the final hydrate structure. If so, it opens an avenue for studying promoters of methane diffusion in the hydrate bulk.

In the present work, we shall study the diffusion barriers associated with hopping from one cage to another, with or without a vacancy in the water ring joining the two cages. We will compute the

Helmholtz energy barrier associated with diffusing between two cages, in the circumstance where either none, one, or both of the cages are occupied with a guest molecule other than the diffusing molecule. We shall do this for all combinations methane, carbon dioxide, nitrogen, and hydrogen.

II. METHOD

A 2x2x2 unit cell sI hydrate was constructed from the proton configuration that generates a minimal electrical dipole moment for a single unit cell as determined by Takeuchi and co-workers[23]. The lattice constant used was 11.99 Å, which was obtained from a brief *NPT* simulation of a completely filled methane hydrate at 100 bar. In all simulations, all cages not directly participating in the hopping event being studied, were filled with methane. The water model used was TIP4P/Ice[24], which is known to yield good estimates for the phase diagrams of ice and hydrates[12,24–28]. Methane, carbon dioxide and methane were modeled with the TraPPE force field[29]. Hydrogen was modeled using the classical potential developed by Alaviet al.[30] to study diffusion in sII hydrates. Lennard Jones interactions were truncated and shifted at 10 Å. Electrostatic interactions were treated with an Ewald summation with a relative precision of 10^{-5}. We have examined the hopping rate using Metropolis Monte Carlo simulations. This choice is simple to implement, and allows us to explore a large set of possible scenarios at cheap computational cost. The hopping between two cages was described by an order parameter, defined as follows: We define $\mathbf{v_r}$ as the vector drawn from the mass center of the initial cage to the mass center of the water ring joining two cages, $\mathbf{v_c}$ as the vector drawn from the mass center of the initial cage to the mass center of the final cage, and $\mathbf{v_g}$ as the vector drawn from the center of the initial cage to the center of mass of the diffusing guest molecule. Then, we define the order parameter ξ describing the hopping between two cages as

$$\xi = (\mathbf{v_g} - \mathbf{v_r}) \cdot \mathbf{v_c}/|\mathbf{v_c}|, \tag{1}$$

i.e. the difference between the projections of $\mathbf{v_r}$ and $\mathbf{v_g}$ onto $\mathbf{v_c}$. Thus, when the order parameter $\xi = 0$, we are located at the interface between the two cages. This definition is similar in nature to the one used by Demurov et al.[15], who defined a plane at the interface between cages by using a least square fit on the position of the water molecules. It is of important that the location of the interface is explicitly used when defining the order parameter. The water molecules in the cages are rather flexible, so the distance between the interface and the center of the cage can

vary by more than 0.5 Å. Because of this, simulations using order parameters that only use the position of the hopping molecule relative to the centers of the two cages, can give misleading results; configurations that possess the same value of the order parameter could be both in front and behind the window. This will result in a severe reduction in the measured free energy barrier.

The free energy difference of two order parameters values ξ_0 and ξ_1 is

$$\Delta F = F(\xi_1) - F(\xi_0) = -k_B T \ln \frac{p(\xi_1)}{p(\xi_0)}, \tag{2}$$

where $p(\xi_0) = <\delta(\xi - \xi_0)>$ is the probability density of measuring the order parameter ξ_0. To obtain accurate statistics, we performed umbrella sampling[31], using infinite square wells with a width of 0.4 Å. Each well overlapped the next well by 0.2 Å. Indpendent simulations consisting of 20000 equilibration cycles, and 100000 production cycles were performed. The samples from the production cycles were subdivided into 5 blocks. From those 5 blocks, 5 different free energy profiles were computed, and the standard deviation between those profiles was computed to estimate the uncertainty in the free energy barrier. In each simulation cycle, 550 attempts were made to move or rotate a molecule. On average, 18% of those moves attempted to move the guest molecule. At the end of each production cycle, the order parameter was recorded. Histograms were merged by matching the overlapping regions. In simulations where an auxilliary molecule was present in one of the two cages involved in the hopping event being studied, that molecule was constrained so that it remained in the same cage throughout the simulations. For simulations where a water molecule was removed from the ring between cages, a sphere with radius 2 Å was defined around the original position of the Oxygen atom of that water molecule. To prevent the water vacancy from healing, we rejected moves that would have lead to the Oxygen atoms of other water molecules from entering that sphere.

III. RESULTS AND DISCUSSION

A. Diffusion involving only a single guest

In figure 2, we have displayed all free energy profiles associated with a guest molecule diffusing between two otherwise empty cages. The barriers, defined as the peak of the energy profile minus the lowest point in the initial cage, are summarised in the first part of figure 3.

As expected, the barriers corresponding to movement through rings with water vacancies in them are significantly lower than the barriers corresponding to intact rings. It is worthwhile to no-
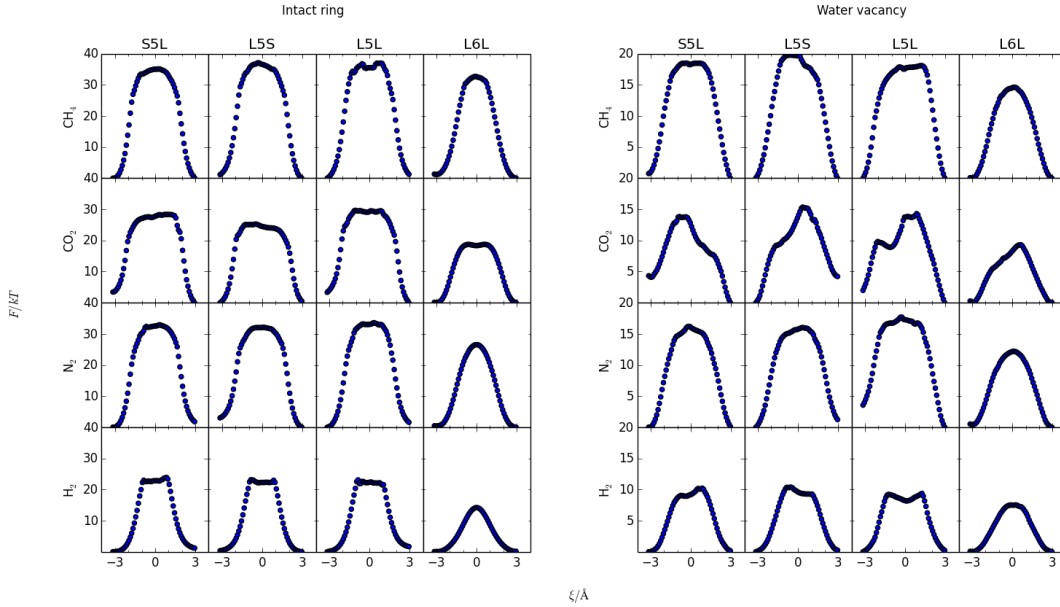
FIG. 2 Free energy profiles associated with guest molecules hopping between two otherwise empty cages. In the left panel, the guests hop through intact rings of water, in the right panel, the guests hop through rings with a single water vacancy.

tice that the barrier associated with hydrogen moving through an *intact* 6-membered ring, is lower than the barrier associated with methane moving through any ring even when a water molecule is missing. The computed barriers for methane and carbon dioxide can be compared to literature values. For methane, the computed values are quite similar to those computed by Peters et al.[10] at 250 K, using TIP4P as a water model. However, neither values correspond well with experimentally determined activation energies for diffusion limited hydrate growth, which range between 52 and 62 kJ/mol[32]. Those values are strictly higher than the free energy barrier associated with methane diffusing through any ring with a water vacancy, and strictly lower than the free energy barrier associated with methane hopping through intact rings. Kuhs et al.[32] have pointed out that this activation energy is similar to the activation energy associated with the diffusion of water in ice. This indicates that for methane, the diffusion is dominated by hops through rings with water vacancies, and rate limited by the time it takes to form such vacancies by internal movement of the water molecules.

The computed values for CO_2 diffusing through windows with vacancies are quantitatively and qualitatively different from those computed by Demurov et al.[15] At 200 K, those authors predicted diffusion barriers of 5.7, 10.1, 6.6, and 7.7 $k_B T$ for the S5L, L5S, L5L, and L6L hops, respec-
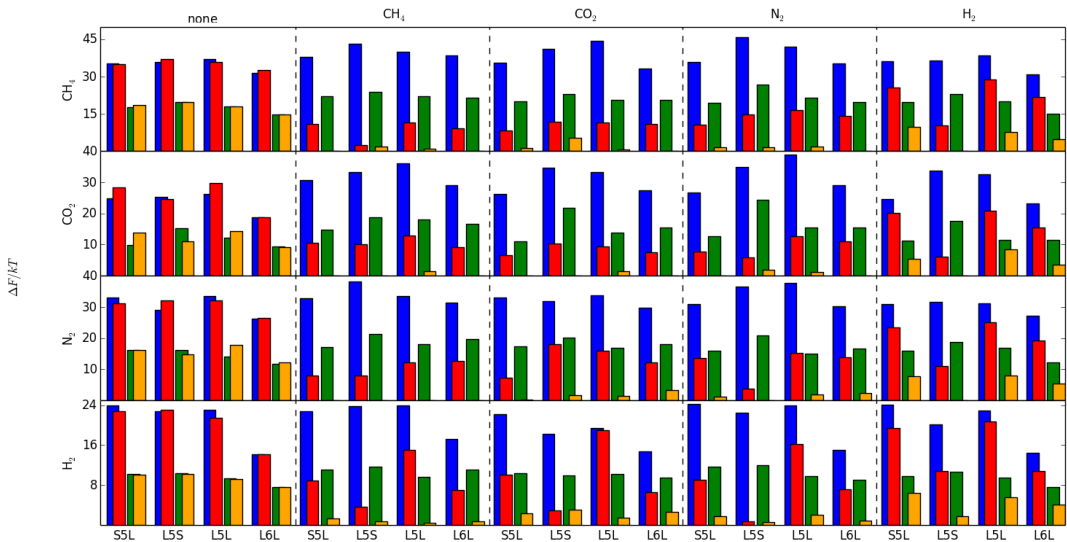
FIG. 3 Free energy barriers associated with hopping from an unoccupied cage into a cage occupied by the molecule listed at the top of the chart. The guest that is hopping is listed on the left side of the chart. At the bottom of the chart, the ring being hopped through is listed. S5L means that the guest is hopping from a small cage through a 5-membered ring into a large cage, L5S is the reverse. L5L and L6L indicates that the guest is hopping between two large cages, through a 5- and a 6-membered ring, respectively. Blue and red bars indicate that the guest is hopping through an intact window. Green and orange bars indicate that the guest is hopping through a window with one water vacancy present. Blue and green bars represent the barrier associated with the guest hopping forward, red and orange represent the barrier associated with the guest hopping backwards through the window.

tively. Extrapolating from 200 K, they predicted a further reduction to 4.14, 6.46, 4.5, and 5.3 $k_b T$ at 273.15 K. In contrast, at 280 K we find barriers of 9.8, 15.5, 12.6, and 9.3 $k_B T$ for those same barriers. Thus, we predict significantly higher barriers than Demurov et al. Also differently to Demurov et al., we predict that hopping through the 6-membered ring is associated with the lowest energy barrier. It is possible that this disparity is due to different choices for molecular models - Demurov et al. had used the SPC/E water model, which certainly is more different from TIP4P/Ice than the TIP4P model used by Peters et al. A different possibility relates to the apparent asymmetry in the barriers computed in our work (the overall free energy barrier via Eq. 2 implies $\xi_1 \neq 0$). To resolve the origin of this asymmetry, we attempted one set of simulations in which a CO_2-molecule without any partial charges. In that set of simulations, the barrier was symmetric

across the interface. For this reason, we conclude that the asymmetry occurs because the hydrogen molecules, that would have formed hydrogen bonds with the removed water molecule, are distributed asymmetrically and interact with the partial charges of CO_2.

Falenty et al.[18] found that the activation energy related to CO_2 diffusing through the hydrate can be divided into two distinct regimes - one regime with a low activation energy of ~ 19 kJ/mol, for temperatures below 225 K, and one regime with a notably higher activation energy of ~ 46 kJ/mol, at temperatures above 225 K. This can be explained as follows[18]. In the high temperature regime, CO_2 can diffuse *without* a water vacancy being present in the rings, while in the low temperature regime, the diffusion is dominated by hops through cages with water vacancies. In fact, that explanation appears to be consistent with our findings, as CO_2 diffusing through an intact 6-membered ring has to overcome a barrier of 18.8 $k_B T$ - which at 280 K corresponds to 43.8 kJ/mol.

The barriers associated with nitrogen hopping through the rings, are consistently higher than for CO_2. This is especially true for hops through the intact 6-membered ring. Here, nitrogen must overcome a barrier of 26.2 $k_B T$, 7.4 $k_B T$ higher than that for carbon dioxide. This difference seems to indicate that nitrogen has more difficulty diffusing through the bulk of the sI hydrate than CO_2. We were not able to find any literature that measures the diffusion of nitrogen in sI hydrates specifically, or in hydrates in general.

The smallest barriers in this work are associated with hydrogen hopping from cage to cage. In fact, hydrogen can hop through an *intact* 6-membered ring faster than methane can hop through a 6-membered ring with a vacancy. It is clear that if there is a small amount of hydrogen present inside the hydrate, it will be able to diffuse through the hydrate at a rapid pace. Hydrogen naturally forms sII hydrates, and the majority of studies of hydrogen diffusion in hydrates have focused on sII and sH hydrates. While we are not aware of any works studying hydrogen diffusion in sI hydrates, it is worthwhile to note that the barrier for hopping through the intact 6-membered ring (14.2 $k_B T$) is comparable to the ~ 32 kJ/mol associated with hydrogen hopping through a hexagonal ring in the sII hydrate[22].

B.   Multiply occupied cages

To obtain further information about the gas exchange process, we have computed the free energy profiles associated with guests hopping into, or out of, a cage that is occupied by another molecule. Examples of how this affects the barrier can be seen in figure 4, in which one cage is
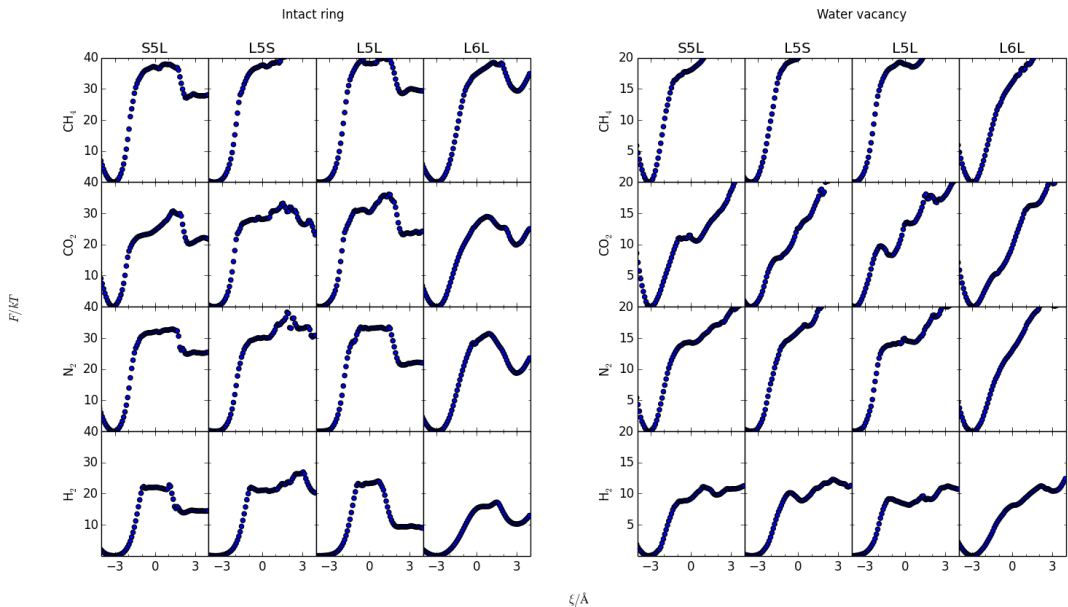

FIG. 4 Free energy profiles associated with guest molecules hopping between between an empty cage and a cage occupied by one methane molecule. In the left panel, the guests hop through intact rings of water, in the right panel, the guests hop through rings with a single water vacancy.

occupied by a methane molecule, and figure 5, where hydrogen occupies a cage. If one of the cages is occupied by carbon dioxide or nitrogen, the free energy profile is qualitatively similar to that of methane occupying the same cage. From figure 4, it is clear that large cages can be doubly occupied in a meta-stable state, provided that there are no water vacancies present. Also small cages appear to have some capacity for double occupancy, although it is clear that two methane molecules are unable to co-inhabit a small cage.

When there is a vacancy present, small cages can not be doubly occupied, as is clear from the lack of a free energy minimum - or even plateau, for the doubly occupied cages. The sole exception to this is when the small cage is doubly occupied by two hydrogen molecules, for which there is a shallow plateau. For large cages, hydrogen appears to be able to co-occupy the cage with any of the other guest molecules, again in a shallow free energy well. It is clear from the remaining free

energy profiles that molecules other than hydrogen are unable to co-inhabit cages when there are water vacancies present.

While they may not be able to co-inhabit cages, it is still possible that two large guests can swap the cages they occupy, using a single window. In support of this possibility, we note that the free energy profile can be decomposed into two segments. In the first segment, the guest is in an otherwise unoccupied cage. Here, the free energy profile is almost entirely determined from the repulsive forces of the water molecules in the ring that connects the cages. Except for CO_2 diffusion, if we compare the free energy at the interface between cages, we find only a small difference between the case where the target cage is unoccupied, and where there is a large guest in the target cage. As an example, we can consider nitrogen moving through a 6-membered ring into a cage occupied by methane. To reach the interface, a free energy barrier of ~ 12 k_BT must be overcome. This is virtually the same as the barrier associated with reaching the interface of an empty cage. In the second segment, the molecule has reached the interface, and must overcome the repulsive forces of the co-occupying guest. Since we have required the other guest to be present in the cage throughout our simulations, this results in yet another slope as the guest tries to enter the center of the cage. If the other molecule was allowed to jump out of the cage, this slope might well be avoided, or at least slightly mitigated. However, studying that would require the use of a more advanced simulation technique that is actually able to study the dynamics of these events, which are not perturbed by artificial constraints. A combination of path sampling with replica exchange[33] would be a way to achieve that.

In this context, it is interesting that nitrogen sees little to no increase of the free energy barrier when the target cage is occupied, while CO_2 sees a sizable increase - especially when passing through the 6-membered ring. For CO_2 entering a cage occupied by methane, the part of the barrier that is associated with reaching the interface increases from 9 to 13 k_BT - a barrier that now is higher than the barrier that nitrogen must overcome. The increase comes about due to the length of CO_2. As CO_2 reaches the interface, its frontmost oxygen atom is already inside the cage, feeling the strong repulsive force of the methane molecule. When the water ring is intact, both N_2 and CO_2 see an increase of the barrier when attempting to enter a cage occupied by methane. For N_2, the L6L barrier increases from 26.2 to 31.3 k_BT, while for CO_2, the barrier increases from 18.8 to 29.0 k_BT. Again, CO_2 sees a comparatively stronger increase of the barrier, although in this case it remains lower than that for N_2. Still, once the cage is doubly occupied, the barrier

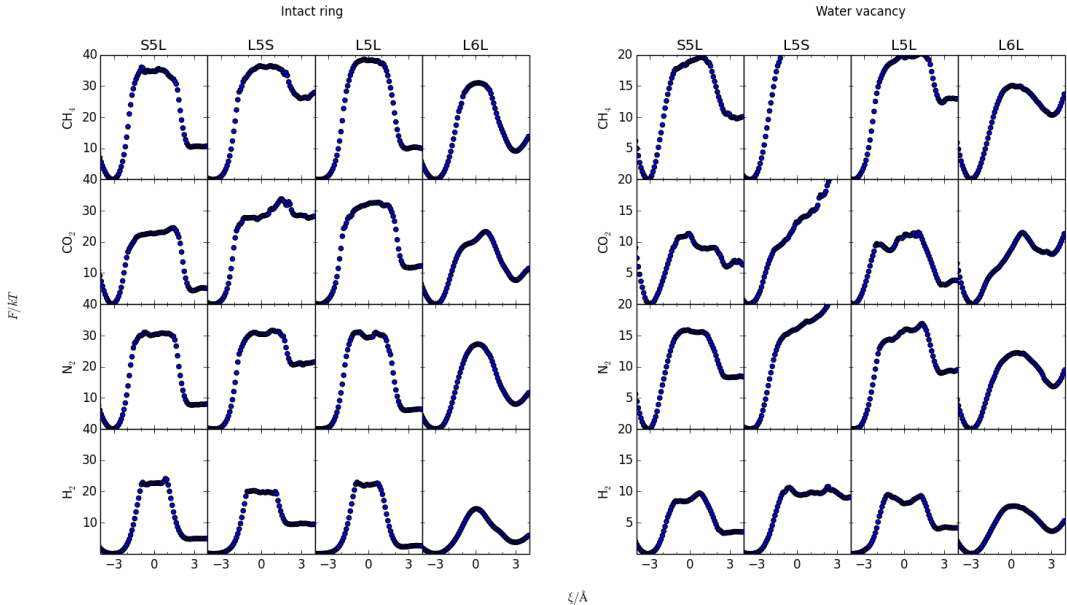associated with hopping back out is higher for nitrogen than carbon dioxide.

FIG. 5 Free energy profiles associated with guest molecules hopping between between an empty cage on the left, and a cage occupied by hydrogen, on the right. In the left panel, the guests hop through intact rings of water, in the right panel, the guests hop through rings with a single water vacancy.

For small cages, the repulsive presence of an occupying molecule is felt far sooner, leading to a noticeable increase in an already high barrier. Unlike the case for the 6-membered ring, the barrier associated with nitrogen entering the small cage remains higher than the barrier associated with carbon dioxide entering. It has been suggested that a mixture of nitrogen and carbon dioxide leads to an improved recovery of methane[2]. Using a mixture of nitrogen and carbon dioxide has been reported to increase the percentage of methane that was harvested in an exchange, relative to using a gas of pure carbon dioxide[3,4,34].

Our results, however, seem not to confirm this. The barrier associated with either nitrogen or carbon dioxide entering a small cage with methane remains prohibitively high. Further, if the exchange process is limited by the diffusion of the gases in the bulk of the hydrate, it is not clear that any preference for small cages is relevant, as diffusion in the bulk of the hydrate can progress without the use of small cages. At best, the free energy barrier associated with diffusion is equal between nitrogen and carbon dioxide, and for the most part, carbon dioxide has a lower diffusion

TABLE I Free energy barriers F/k_BT associated with hopping from an otherwise empty cage through an intact water ring or through a ring with water vacancies.

	Intact window				Single water vacancy			
Guest	L5S	S5L	L5L	L6L	L5S	S5L	L5L	L6L
Hopping into empty cage								
CH_4	17.9 ± 0.4	19.8 ± 0.3	18.5 ± 0.8	14.7 ± 0.1	36.0 ± 0.9	36.5 ± 0.8	38.0 ± 0.8	31.7 ± 0.6
CO_2	9.8 ± 0.6	15.5 ± 0.3	12.6 ± 0.8	9.3 ± 0.2	25.1 ± 2.0	25.8 ± 0.5	27.1 ± 1.0	18.8 ± 0.1
N_2	16.3 ± 0.2	16.1 ± 0.3	14.5 ± 1.0	11.8 ± 0.2	33.4 ± 0.7	30.0 ± 1.0	34.8 ± 0.8	26.2 ± 0.1
H_2	10.2 ± 0.5	10.4 ± 0.2	9.4 ± 0.2	7.5 ± 0.2	24.0 ± 0.1	22.9 ± 0.4	23.1 ± 0.7	14.2 ± 0.1
Hopping into cage occupied by methane								
CH_4	22.4 ± 0.6	24.0 ± 0.4	22.2 ± 0.5	21.5 ± 0.3	38.4 ± 0.5	44.1 ± 1.0	40.6 ± 0.7	38.7 ± 0.5
CO_2	14.9 ± 0.6	19.3 ± 0.6	18.3 ± 0.7	16.7 ± 0.5	31.6 ± 1.0	33.7 ± 0.7	36.2 ± 0.4	29.3 ± 0.6
N_2	17.2 ± 0.5	21.4 ± 0.7	18.4 ± 0.4	19.7 ± 0.4	33.2 ± 0.4	39.4 ± 0.6	34.2 ± 1.3	31.4 ± 0.2
H_2	11.2 ± 0.5	11.7 ± 0.1	9.6 ± 0.2	11.0 ± 0.3	22.9 ± 0.5	24.4 ± 0.7	24.0 ± 0.2	17.2 ± 0.2
Hopping into cage occupied by carbon dioxide								
CH_4	20.1 ± 0.4	23.1 ± 0.6	20.9 ± 1.1	20.8 ± 0.3	36.6 ± 0.8	41.8 ± 0.6	44.5 ± 0.4	33.7 ± 0.5
CO_2	11.1 ± 0.5	22.1 ± 0.8	14.0 ± 0.4	15.6 ± 0.5	26.7 ± 0.7	35.0 ± 0.7	33.8 ± 1.0	27.6 ± 0.2
N_2	17.4 ± 0.2	20.4 ± 0.6	16.9 ± 0.6	18.0 ± 0.1	33.4 ± 0.5	32.2 ± 0.4	33.9 ± 0.3	29.8 ± 0.3
H_2	10.4 ± 0.3	9.9 ± 0.4	10.2 ± 0.5	9.5 ± 0.2	22.4 ± 0.3	18.2 ± 0.2	19.4 ± 0.3	14.7 ± 0.1
Hopping into cage occupied by nitrogen								
CH_4	19.6 ± 0.4	26.9 ± 0.9	21.7 ± 0.7	19.8 ± 0.2	36.4 ± 0.5	46.4 ± 0.5	42.9 ± 0.7	35.4 ± 0.3
CO_2	12.7 ± 0.2	24.6 ± 0.7	15.8 ± 1.1	15.5 ± 0.3	27.1 ± 0.5	35.3 ± 1.1	39.5 ± 1.2	29.2 ± 0.2
N_2	16.1 ± 0.4	20.8 ± 0.5	15.2 ± 0.2	16.6 ± 0.3	31.4 ± 0.5	37.4 ± 0.6	38.4 ± 1.3	30.2 ± 0.2
H_2	11.7 ± 0.2	12.0 ± 0.2	9.8 ± 0.6	9.0 ± 0.2	24.4 ± 0.4	23.9 ± 0.9	24.2 ± 1.0	15.1 ± 0.0
Hopping into cage occupied by hydrogen								
CH_4	19.8 ± 0.3	23.0 ± 0.2	20.5 ± 0.5	15.1 ± 0.1	36.5 ± 0.7	37.9 ± 0.7	39.7 ± 0.5	31.5 ± 0.5
CO_2	11.4 ± 0.4	17.7 ± 0.6	11.8 ± 0.4	11.5 ± 0.2	25.2 ± 0.5	34.1 ± 0.5	32.8 ± 0.5	23.3 ± 0.1
N_2	15.9 ± 0.3	18.9 ± 0.3	17.1 ± 0.7	12.2 ± 0.1	31.1 ± 0.3	32.4 ± 0.4	31.5 ± 0.3	27.3 ± 0.3
H_2	9.7 ± 0.3	10.6 ± 0.4	9.5 ± 0.1	7.6 ± 0.2	24.2 ± 0.1	20.7 ± 0.7	23.0 ± 0.2	14.4 ± 0.1

barrier. This is independent of whether the molecules are diffusing into small or large cages. Especially if the diffusion is dominated by molecules hopping into empty cages, we would not expect nitrogen to have any advantage over carbon dioxide. At most, it seems like nitrogen is equally good or better than carbon dioxide at entering cages that are occupied by methane.

However, the story is different for hydrogen. From figure 3, it is clear that hydrogen is able to enter occupied cages, both through intact rings, and rings with water vacancies. For intact rings, entering a cage through an intact 5-membered ring is associated with a barrier of less than 24 $k_B T$. This is roughly the same barrier that is associated with the diffusion of water in ice. Entering through intact 6-membered rings is associated with a barrier of 14-16 $k_B T$. As such, it appears that hydrogen can diffuse freely, without having to wait for defects to form. When hydrogen is present in a large cage, it reduces the barrier associated with the other guest hopping out, by $\sim 10\ k_B T$. This reduction is somewhat smaller than the reduction that occurs when a vacancy forms in the water rings between cages, but large enough that the barriers associated with the L6L hop through intact cages is reduced to $\sim 20\ k_B T$, for all guests considered. Thus, it appears that the introduction of hydrogen is able to increase the speed of guests diffusing through the bulk of the hydrate which agrees with the experimental works of Ding et al[6]. The amount of hydrogen required to achieve this boost is small, of the same order as the amount of water vacancies in the hydrate structure.

IV.   CONCLUSION

In the present work, we have computed the free energy barriers associated with methane, carbon dioxide, nitrogen, and hydrogen hopping through rings of water between the cages of the sI hydrate structure. The barriers have been computed for intact rings, as well as rings with single water vacancies in them. We have computed the barriers associated with guests hopping into cages that are already occupied by other molecules. We show that hopping into occupied large cages through intact rings is associated with a small to negligible increase in the barrier associated with diffusion. For hopping into large cages through rings with vacancies, our work suggests that the same is true, but more advanced simulation techniques are required to understand the exact dynamical implications[33]. With the exception of hydrogen, hops into occupied small cages appears to be prohibited. The work suggests that nitrogen is more capable than carbon dioxide of diffusing into

large cages that are already occupied by methane, but only weakly so. This is a possible reason for a reported increase in the amount of methane harvested when the methane-carbon dioxide exchange is attempted with a mixture of nitrogen and carbon dioxide. Only hydrogen is capable of coexisting in small cages with any of the other molecules. Improvements in the amount of methane harvested when using a mixture of carbon dioxide and hydrogen[6] appears to be linked with a boost of the bulk diffusivities of both methane and carbon dioxide.

V.   ACKNOWLEDGEMENTS

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