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Complete List of Authors:	Trinh, Thuat; NTNU, Department of Chemistry Waage, Magnus; Norwegian University of Science and Technology, Department of Chemistry van Erp, Titus; Norwegian University of Science and Technology, Department of Chemistry Kjelstrup, Signe; Norwegian University of Science and Technology, Department of Chemistry

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Low barriers for hydrogen diffusion in sII clathrate

Thuat T. Trinh,^{a,‡} Magnus H. Waage,^{a,‡} Titus S. van Erp,^a and Signe Kjelstrup^{*a,b}

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The transport of gas molecules in hydrates is presently poorly understood. In sII structured hydrates with hydrogen guests there is, for instance, a mismatch between experimental and computed values for diffusion constants. We provide an explanation for the experimentally observed diffusion rates, using DFT-based molecular dynamics simulations at 100 K. By considering the effect of cage occupancy, as well as the flexibility of the water lattice, we show that barriers for hydrogen diffusing between cages, can approach values as low as 5 kJ/mol, which is very close to experimental values.

A clathrate structure consists of hydrogen bonded water cages, stabilized by guest gas molecules.¹ Mao et al.² demonstrated that hydrogen can be trapped in sII hydrate structures, spurring investigations into hydrates as a storage medium for H₂. Florusse et al.³ showed that the inclusion of THF as a promoter molecule allowed such hydrates to form at ambient conditions. This, however, came at the cost of most of the storage capacity. Lee et al.⁴ found that this cost could be tuned by varying the content of THF. In order for the hydrate to be usable as a storage medium, low barriers for gas diffusion are required. NMR studies⁵ and decomposition studies⁶ with tetrahydrofuran (THF) have produced diffusion barriers as low as 3 kJ/mol, but this contrasts the rather large barriers found by molecular simulations^{7,8}. The purpose of this paper is to investigate this discrepancy.

In the sII structure, the single unit cell contains 136 water molecules held together by hydrogen bonds, forming 8 large (L) and 16 small (S) cages, see Fig. 1. A guest molecule diffusing through the structure will need to pass through the pentagonal (p) or hexagonal (h) windows between cages. Three types of jumps can be distinguished, two related to pentagonal and one type related to hexagonal windows. Through pentagonal windows, jumps can take place between small cages, or between a large and a small cage. These jumps will be denoted SS(p) and LS(p), respectively. A jump

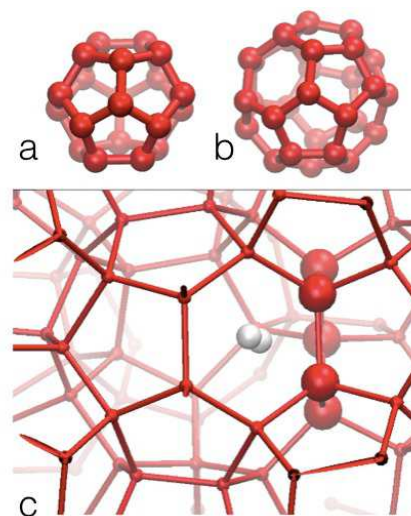


Fig. 1 a,b, Structure of the small S, and large L cages that make up the sII clathrate structure. For clarity, only oxygen atoms are shown. c, Snapshot of a H₂ molecule traveling from the centre of a large cage towards a pentagonal interface leading to a small cage. For clarity, the H₂ molecule and the oxygen molecules of the pentagonal window are shown by their van der Waals radii only; the other molecules being pictured in a suppressed form.

through hexagonal windows can only take place between large cages and is denoted LL(h).

The variation in Helmholtz energy along the path between two cage centers can be used to assess the probability for cage jumping, and thus the rate of diffusion. In a classical molecular dynamics (MD) simulation, the frequency of jumps was used to give a rough estimate of the energy barrier associated with the LL(h) transition. The value, 32 ± 12 kJ/mol,⁷ was supplemented with static calculations, yielding energy barriers of around 20 and 30 kJ/mol for jumps through the LS(p), and LL(h) windows, respectively.⁷ Static DFT studies have reported a similar qualitative behavior, although the reported energy barriers are smaller, particularly for the jumps through pentagonal cages. Depending on the orientation of the hydrogen molecule upon transfer, the barrier for SS(p) was 99 or 118 kJ/mol for the perpendicular and parallel orientation.⁸ For LL(h) the same orientations gave 23 and 30 kJ/mol, re-

^aDepartment of Chemistry, Norwegian University of Science and Technology, Høgskoleringen 5, 7491-Trondheim, Norway

^bProcess and Energy Department, Delft University of Technology, Leeghwaterstraat 39, 2628 CB Delft, The Netherlands

‡Equal contributor

spectively. THF is known to exclusively occupy large cages, implying that hydrogen jumps solely between pentagonal windows.⁹ Since this is associated with a high barrier, the experimental data have so far remained unexplained.

In order to reduce the discrepancy between experimental and computational values, we here include the dynamic motion of the water cage and guest molecules in the ab-initio MD simulations. Further, we study how the diffusion barriers are affected by inclusion of more than one occupant in the cages.

Simulations were done with a periodic cubic box of 17.047\AA representing the sII unit cell. The 136 initial oxygen coordinates were taken from X-ray measurements.¹⁰ The orientation of the hydrogen bonds was set to obey the Bernal-Fowler rules for ice.¹¹ Hydrogen molecules were randomly positioned and oriented in the cage being studied, a minimal distance from each other and the water molecules. Other cages were kept empty. In the ab-initio MD simulations, we applied a 0.5 fs time step in the DFT-based Born-Oppenheimer molecular dynamics integrator, using the Quickstep package¹² in the CP2K program.¹³ We selected the BLYP exchange-correlation functional,^{14,15} which has proven to yield accurate water dynamics^{16,17} with a local DZPM basis set, in addition to a plane wave basis sets with an energy cutoff of 400 Ry, and Goedecker-Teter-Hutter (GTH) pseudopotentials^{18,19} for description of core electrons. A Grimme's type correction²⁰ was used to describe the van der Waals interactions and Nosé-Hoover thermostat chains were used²¹ to keep the temperature at 100 K. To obtain $\Delta E(0\text{K})$, the geometry-optimized energies at the window and x_{min} were used.

The Helmholtz energy $A(x)$ was calculated as a function of the distance between the center of the hexagonal or pentagonal window and the center of mass of hydrogen, by thermodynamic integration of the averaged constrained force along the path²¹. A distance was set, and the state corresponding to this distance was generated with constrained molecular dynamics simulations, each simulation point lasting 10 ps. Around 10 points along x were produced in this manner, amounting to a total simulation time of about 100 ps. The value of $A(x)$ incorporates contributions to the entropy from lattice vibrations and rotational degrees of freedom of all present H_2 .

To complement the ab-initio MD simulations, we performed Monte Carlo simulations with umbrella sampling²¹ using classical force fields for water²² and hydrogen²³ structures, where the water lattice structure either was flexible, or kept fixed, meaning that movement was allowed, or disallowed, respectively. The hydrogen molecule was initially positioned in the cage center, and a simulation consisting of 10,000 equilibration cycles and 200,000 sampling cycles was started. Each cycle included one attempted rotation and translation per molecule. After the first simulation, a new simulation was performed, in which a barrier restricted the movement of the hydrogen molecule. The barrier ensured that the

hydrogen molecule stayed in the area that was less than 20% likely in the preceding simulation. This process was then repeated until the entire range between the cage center and the cage window had been examined, at which point the histograms were combined to find the probability distribution of being at position x . The Helmholtz energy was then obtained from $A(x) = A(x_{min}) - RT \ln p(x)$, where x_{min} was the local minimum of A .

The resulting profiles of the Helmholtz energy are shown for the various cases for $0 < x < 3.0\text{\AA}$ in Figures 2 and 3. The barrier, which can be linked to the probability of a jump between cages, is $\Delta A = A(0) - A(x_{min})$, where 0 indicates that the molecule is at the window between cages, and x_{min} means that the molecule is in the Helmholtz energy minimum of the cage. The position of this minimum depends on the occupancy, as well as the shape of the cage. The corresponding internal energy difference ΔE was calculated from average potential energies at x_{min} and the window in NVT -constrained simulations. The uncertainty of this energy difference was found from linear combination of the uncertainties at each point, and is 2 kJ/mol. The entropy contribution was found at 100 K from $T\Delta S = \Delta E - \Delta A$ (see Table 1). All free energy results are expressed in terms of Helmholtz energies, but one can assume that results for the Gibbs energy are the same, since the enthalpy (H) in good approximation is equal to the internal energy (E) due to the low compressibility of clathrates.²⁴

The barriers for jumping through a hexagonal window were always smaller (4-6 times) than barriers for transport through pentagonal windows. The values of ΔA compare well with ΔE from static DFT calculations, but only for pentagonal windows.^{8,25,26} The high barrier for transport through pentagonal windows is in agreement with listed literature data for fixed structures. The barrier is slightly lower for LS(p) than for SS(p), 53 kJ/mol and 59 kJ/mol, respectively (Fig. 2 a). The barriers for SS(p) and SL(p) are equivalent to each other. The paths from the cage minima to these two windows are symmetrical if we only consider the water molecules of the small cage. The different structures of the target cages does not appear to have much influence on the barrier, indicating that the primary contribution to the barrier height is the shape of the cage window. For the classical simulations, keeping the water lattice fixed yields a Helmholtz energy barrier of 29.5 kJ/mol for the LL(1H₂(h)) transition, similar to the 30 kJ/mol reported for static calculations⁷. For the flexible lattice, this barrier is reduced to 22.5 kJ/mol. The fixed-framework approximation thus results in an overestimation of the barrier by 7 kJ/mol.

As shown in Fig. 2 and Table 1, the barriers decrease even further as the occupancy of the cage increases. This applies already to pentagonal windows (a), but to a larger degree to hexagonal windows (b), when the occupancy is increased above 4 guests. We have included cases where the occupancy

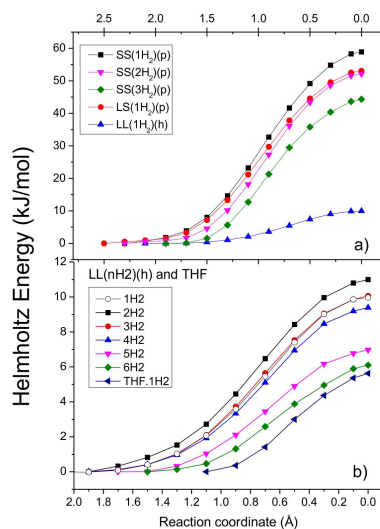


Fig. 2 a, b, Helmholtz energy profile of half the path between two cages for H_2 diffusion from a large or small cage through a pentagonal (p) or hexagonal (h) window to another cage. Also shown is the effect of having multiple hydrogen occupancy in the small cage (a) and the effect of multiple hydrogen occupancy or the presence of THF in the large cage when diffusing through the hexagonal window (b)

of the cage is larger than that observed in experiments (more than 2 H_2 molecules in a small cage, more than 4 H_2 molecules in a large cage, co-occupancy of THF and H_2). However, these states may exist as metastable states. For pentagonal windows, increased occupancy decreased the barrier peak by as much as 20 % relative to when the transported H_2 molecule is alone in the cage, while a relative decrease of as much as 50 % was found for the hexagonal window (the barrier was lower in the outset). Clearly, the presence of THF in large cages is able to lower the barrier to transport for LL(h) jumps more than any possible amount of hydrogen (up to an occupancy of 6 hydrogen molecules), see Fig. 2-b. From these results, we conclude, that hydrogen molecules can use the path between large cages as lanes of transport, despite the presence of THF molecules. We have found that a dynamic model for transport, at 100 K, can lower the barrier to a value of 5 kJ/mol, which is very close to the experimental value of 3 kJ/mol, reported in systems above 250 K.⁵ We expect a further reduction of the barrier with increasing temperatures. The barrier is reduced because the energy level associated with being in the center of the cage is increased, as more guests are added. Conversely, near the cage window, the hydrogen molecule is no longer affected as much by the other molecules in the cage. For this reason, we have not included the impact of guests in the neighboring cages in the ab-initio MD simulations. This was examined by performing classical simulations for the case

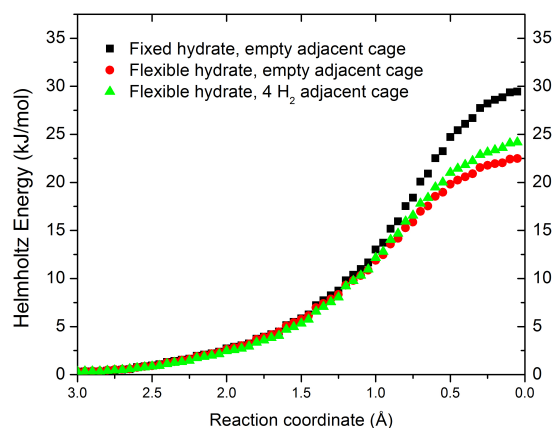


Fig. 3 Helmholtz energy profile of half the path between two large cages, calculated from classical force fields. The hydrogen molecule is alone in its current cage and is transported to an adjacent cage with either 0 or 4 H_2 molecules present. The water lattice of the hydrate is either kept fixed, meaning that the water molecules are not allowed to move, or flexible, meaning that the water molecules are allowed to be translated or rotated.

of a single hydrogen molecule moving into a cage occupied by either 0 or 4 other hydrogen molecules, *c.f.* Fig. 3. The resulting barrier was 24.1 kJ/mol, a modest increase from the 22.5 kJ/mol found when the neighbouring cage was empty.

The results obtained are supported qualitatively by earlier findings. The $\Delta E(0K) = 63$ kJ/mol for SS(p)/SL(p) agree qualitatively with the 72 kJ/mol reported by Li et. al²⁵ whereas Alavi and Ripmeester⁸ reported somewhat higher values of 99 and 118 kJ/mol for the transfer of hydrogen, oriented perpendicular or parallel to the window plane, respectively. The result $\Delta E(0K) = 22$ for LL(H_2)(h) is furthermore in good agreement with the range of values (24-29 kJ/mol) reported in refs.^{8,25,26}

The molecular orientation of the hydrogen is shown in Fig. 4 for pentagonal windows (a) and hexagonal windows (b). The figure shows the probability distributions for cosine of the angle θ , indicating the orientation of molecule with respect to the window plane, with $\theta = 0$ representing the parallel position. The angle-distribution is more or less uniform when hydrogen is in the center of the cage, but also when it is at the hexagonal window, while there is a clear peak at lower angles at the pentagonal window. This shows that the hexagonal window allows the molecule to pass independently of its orientation, while the pentagonal window is too small to allow the hydrogen to pass when its axis is not perpendicular to the windows plane. This agrees with a negative value of ΔS in Table 1 for the pentagonal transfer, and with zero or

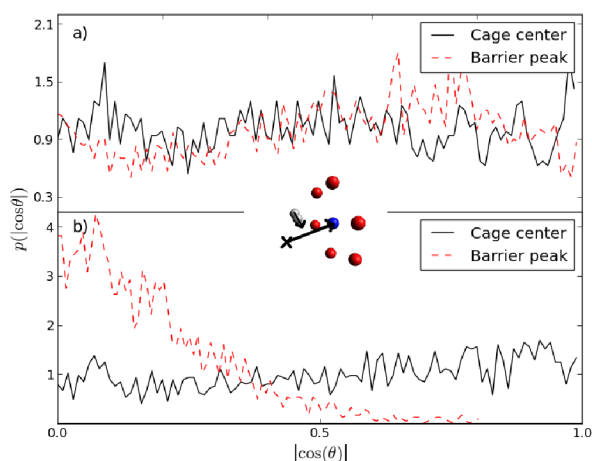


Fig. 4 Distributions of the angle θ between the axis of the H_2 molecule and the window plane, as sampled at the cage center (solid line) and at the barrier peak (red dashed line) for a) hexagonal and b) pentagonal windows. The angles are determined by taking the dot product of the vector between two hydrogen atoms and the vector from the cage center to the center of the cage window, as is illustrated in the insert.

slightly positive values for the hexagonal window, at least for the cases with low occupancy. The different behaviors are also reflected in the relative distortions of the cage windows. When the hydrogen molecule is at the window, the hydrogen bond length in the pentagonal window is increased by 13%, while the same distance only increases by 3% at the hexagonal window. The effect of entropy appears moderate. In order to understand the relatively small $T\Delta S$, one must consider that the Helmholtz energy calculation includes entropy contributions from the whole water lattice plus the hydrogen guest. Movement of water will by far be the dominating contributor to S , masking the effect of single hydrogen molecules. However, the energy difference ΔE reduces at the higher temperature. As the temperature increases, the number of accessible states in configuration states increases equally at both the cage center, and the cage windows. However, the energy associated with these newly accessible states is noticeably higher when the guest is positioned near the cage center, than when it is at the window. For this reason, zero-temperature simulations appear to grossly overestimate the diffusion barrier.

The results of this study suggest that diffusion of hydrogen through the hexagonal windows of sII clathrates is probable, also when the large cages are filled with large molecules, such as THF. In these cases, the molecule must first overcome the relatively high barrier of a pentagonal window between the large and the small cage. After this, the use of large cages as channels allows for rapid transport over distances. Multiple occupancy lowers the transport barrier. The low barrier,

Table 1 Helmholtz energy barrier, ΔA , with energy, ΔE , and entropy contribution $T\Delta S$ of 1-6 molecules of H_2 or THF in sII clathrates as calculated with ab initio MD at 100 K. The last column gives the energy barrier at 0 K.

	kJ/mol	ΔA	$T\Delta S$	$\Delta E(100K)$	$\Delta E(0K)$
SS(p)/SL(p)	59	-2	57	63	
SS(2H ₂)(p)	52	-1	51	51	
SS(3H ₂)(p)	44	-4	40	41	
LS(1H ₂)(p)	53	-5	48	54	
LL(1H ₂)(h)	10	0	10	22	
LL(2H ₂)(h)	11	1	12	29	
LL(3H ₂)(h)	10	-4	6	24	
LL(4H ₂)(h)	9	-1	8	25	
LL(5H ₂)(h)	7	-3	4	20	
LL(6H ₂)(h)	6	2	8	24	
(THF, 1H ₂)(h)	5	0	5	20	

ers, in agreement with experimental findings, can be explained by allowing for the movement of water molecules. The hydrate flexibility, molecular rotations, and cooperative effects, will probably make it possible for hydrogen to diffuse faster through clathrate hydrates. The findings are in contrast to earlier results based on classical or DFT computations done with a fixed water framework. For low temperatures, quantum tunneling can increase the diffusion rate⁸. At the ambient temperatures desired for hydrogen storage, tunnelling should be of less importance.

The findings could be important for future applications of hydrates. Relevant to the issue of hydrogen storage, is that measured diffusion rates can be understood. THF may prevent hydrogen molecules from occupying large cages in a stable hydrate. However, the existence of metastable states means that transport process may still happen using large cages as channels. In general, we show that it is necessary to allow for a flexible hydrate framework in the study of diffusion in hydrates.

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