

Ab *initio* Mechanistic Insights into the Stability, Diffusion and Storage Capacity of sI Clathrate Hydrate Containing Hydrogen

Ahmed Omran^a, Nikolai Nesterenko^b, Valentin Valtchev^{c,*}

^aNormandie Université, ENSICAEN, UNICAEN, Laboratoire Catalyse et Spectrochimie (LCS), 14050, Caen, France

^bTotal Research and Technology Feluy, Zone Industrielle C, 7181 Feluy, Belgium

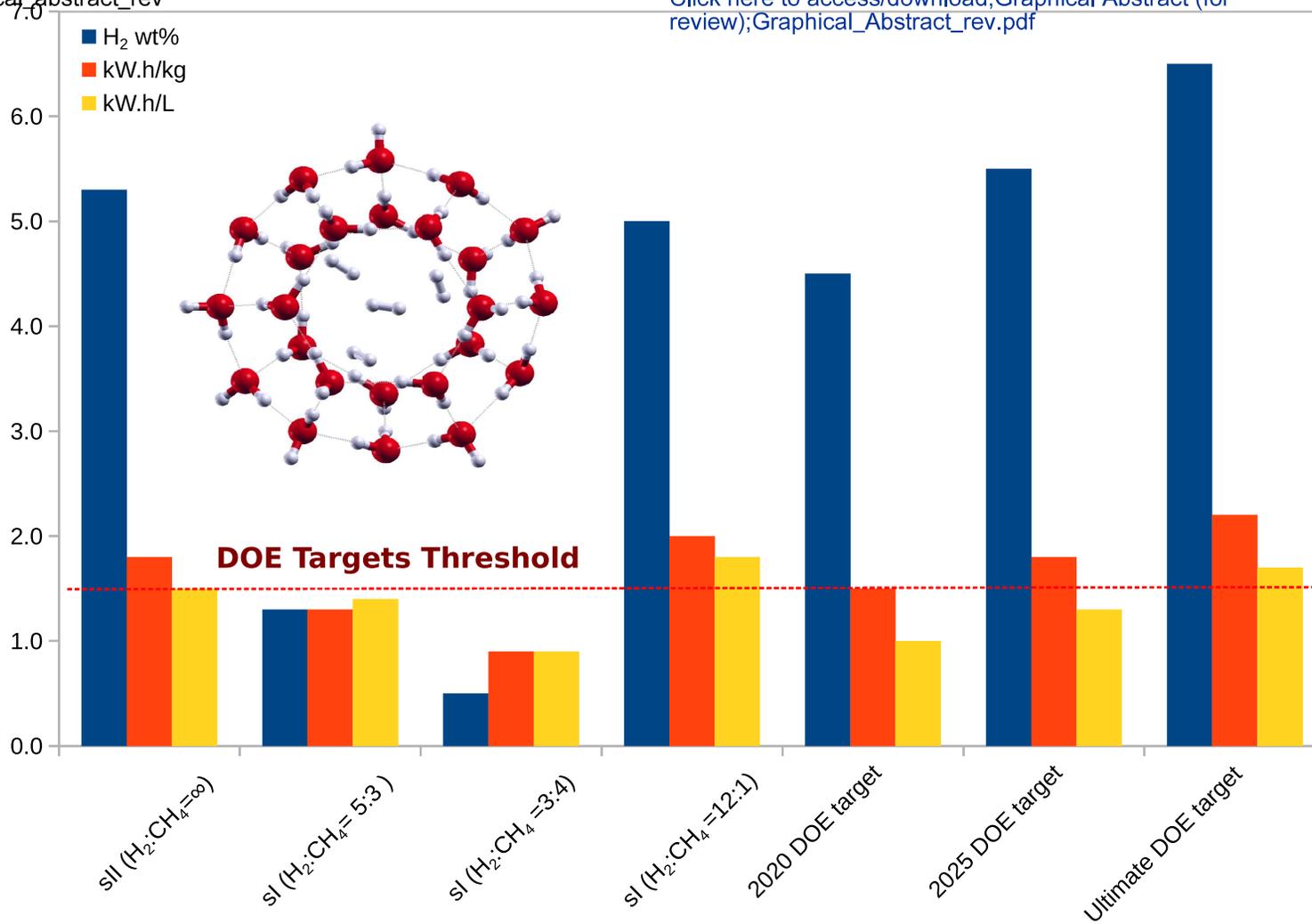
^{c,*}Normandie Université, ENSICAEN, UNICAEN, CNRS, Laboratoire Catalyse et Spectrochimie (LCS), 14050, Caen, France

*To whom correspondence should be addressed:

(Valentin Valtchev) valentin.valtchev@ensicaen.fr; Tel: +33 (0)2 31 45 27

Highlights

- CH₄ works as a thermodynamic promoter to stabilize clathrate for hydrogen storage.
- Clathrate stability is improved by a double occupancy (H₂ - CO₂) of the large cage.
- Double occupancy of the large cages facilitates H₂ diffusion.
- (H₂-CH₄) energy storage in sI are estimated to be 2.0 kW.h/kg and 1.8 kW.h/L.
- (H₂-CH₄) sI capacity meets DOE targets of volumetric and gravimetric energy storage.



Ab *initio* Mechanistic Insights into the Stability, Diffusion and Storage Capacity of sI Clathrate Hydrate Containing Hydrogen

Keywords:

sI hydrate , H₂-CH₄ hydrates, hydrogen storage, diffusion , DOE targets

Abstract

Gas hydrates are non-conventional materials offering great potential in capturing, storage, and sequestration of different gases. The weak Van der Waals interactions between a gas molecule and the pore walls stabilize these non-stoichiometric structures. The present article reports an *ab initio* improved van der Waals density functional (vdW-DF2) study devoted to the interactions associated with H₂, CH₄, and CO₂ adsorption in sI clathrate hydrate. The study provides the clathrate stability, diffusion, and energy storage of possible mixed gas occupancy in sI cages in the presence of H₂. The results also provided the hydrogen energy landscapes and the estimated diffusion activation energy barriers to the large and small cage to be 0.181 and 0.685 eV, respectively. In addition, the results showed that the presence of CH₄ or CO₂ could enhance the storage capacity, thermodynamic stability, and hydrogen diffusion in sI clathrates. The

volumetric storage, gravimetric storage, and molecular hydrogen content in H₂-CH₄ binary sI clathrate are calculated to be 2.0 kW.h/kg, and 1.8 kW.h/L, and 5.0 wt%, respectively. These results are comparable to DOE targets of hydrogen storage.

1 Introduction

Clathrate hydrates are non-stoichiometric “ice-like” structures or inclusion compounds that are formed out of water molecules connected by H-bonding to form three-dimensional cavities which are stabilized by presence of gases such as CH₄, H₂, CO₂, O₂, Ar, Kr and others. The non-stoichiometric nature of clathrates is illustrated by statistical-mechanical analysis of their stabilities which showed that the cages are not completely occupied [1, 2]. The existence of clathrates can be tracked to early 1810 when Sir Humphrey Davy described chlorine gas crystal structure [3]. According to Makagon, the discovery of gas hydrates dates back to 1778-1780. It should be related with the work of the English naturalist Joseph Priestly who described water “impregnated” SO₂ [1]. However, it was not before 1930s when hydrates attracted more attention with the discovery and improvements in the oil and gas industry [4]. At that time, the research was focused on preventing the blockage of pipelines by forming hydrates that can interrupt the production and cause safety concerns [5].

The studies on gas hydrate are related to many fields such as astrophysics [6], geosciences, chemical and petroleum engineering [7]. In addition, gas hydrates have many practical applications that includes but not limited to desalination [8], CO₂ sequestration [9], gas separation [10] and storage [11]. The latter two applications are in the focus of the present article. With the energy transition toward renewables and decarbonization, the focus of current studies on gas

hydrates is shifted equally toward to main areas: (1) their natural occurrence and environmental impact [12–14] (2) the potential technological applications in energy transition and the energy-water nexus [3]. A promising technological applications of clathrates is their usage as energy storage material to store and transport energy gases such as methane and hydrogen in moderate pressure and temperature conditions [15]. Moreover the double-benefit of replacing CH₄ in discovered hydrate reservoirs by the more stable CO₂ clathrates is the focus of intense research [16]. The different interactions between host and guest molecules (host-host, host-guest, and guest-guest) are important to understand their formation, stabilization and dissociation [17].

There is a number of clathrate structures as the most common hydrates are sI, sII, and sH. Similar to other crystalline solids, the clathrate structure formation depends on factors such as pressure, temperature, and the nature of guest species [3]. For example, methane can form sI below 120 MPa. Increasing the pressure to 250 MPa, sII clathrate is obtained, and a further increase to 600 MPa will transform that structure to sH [18]. sI exhibits space group $Pm\bar{3}n$ and the unit cell consists of 46 water molecules. The water molecules are arranged in two kinds of cages - two small cages of pentagonal dodecahedra (5^{12}), and 6 large cages of tetrakaidecahedra ($5^{12}6^2$). The sII includes 136 water molecules arranged in sixteen (5^{12}) and eight hexakaidecahedra ($5^{12}6^4$) with space group of $Fd\bar{3}m$ and lattice parameter of 17.3 Å [3, 19, 20]. Reported to be isostuctural with hexagonal clathrasil dodecasil-1 H, sH showed smaller unit cell of only 34 water molecule but with 3 different sizes of the cages: 3 small (5^{12}), 2 medium irregular dodecahedra ($4^35^66^3$) and a large icosahedra ($5^{12}6^8$) cages [21]. SI clathrate can not accommodate organic promoters and usually encapsulate single gas species such as CH₄ or CO₂ at relatively high pressures. On

the other hand, the other two structures are commonly synthesized as binary clathrates such as hydrogen-tetrahydrofuran (H_2 -THF) [22] and methane-cyclooctane (CH_4 -Cyclo-O) [23] at more moderate conditions on the expense of storage capacity. For example, while pure methane sI clathrate can store about 172 v/v, the maximum storage capacity of binary CH_4 -THF sII can reach approximately 112 v/v only [1].

Hydrogen clathrates are an attractive opportunity for green mass storage, representing a cheap alternative to the metal-organic frameworks (MOFs) or metal hydrides [24]. In 1999, Dyadin *et al.* found experimentally that pure hydrogen clathrate can be synthesized in the form sII clathrate but at very high pressures (≈ 1.5 -2 kbar) [25]. Mao *et al.* showed that the sII hydrogen clathrate is structurally stable up to 145 K at ambient pressure [26]. The estimated storage capacity of the synthesized pure sII hydrogen hydrates is approximately 5.3 wt% at those significantly elevated pressures. Such a hydrogen weight content will result in volumetric and gravimetric energy storage capacities of 1.8 kW.h/kg and 1.5 kW.h/L, respectively [27,28]. The above estimation is based on the double occupation of small (5^{12}) and quadruple occupation of large ($5^{12}6^4$) cages of sII clathrate.

However, the above P - T conditions are extremely demanding and difficult to scale-up. One way to solve that is to use thermodynamic hydrate promoters (THP). In that context, H_2 -THF binary clathrates have been widely studied with the goal to bring the formation conditions to reasonable ranges. Liu *et al.* found that the hydrogen storage capacity in H_2 -THF binary clathrates falls in between 1.6 wt% and 3.8 wt% [29]. Experimentally, storage capacity has been significantly reduced to about 1 wt% since H_2 enclathration is limited

to 5^{12} small cages, while the $5^{12}6^4$ large cages are occupied by THF [30, 31]. For example, Talyzin could not exceed 0.2 wt% in H_2 -THF- H_2O when different pressures for 6 days [32]. Lee *et al.* suggested that the reducing of THF concentration would allow hydrogen storage in large cages in relatively moderate conditions [22]. Although supported by Sugahara *et al.* data [33], this approach was reported non-reproducible by other studies including the one by Strobel *et al.* Thus, boosting the hydrogen capacity upon reasonable pressure-temperature conditions remains a challenge far from being met.

Another direction to solve this problem is to use gaseous thermodynamic promoter of high calorific value and hydrogen content or "blue hydrogen storage". Recently, storing hydrogen along with methane has attracted attention as they are anticipated to meet the US Department of Energy (DOE) targets of energy density while showing affordable formation and storage conditions [26]. Skiba *et al.* studied X-ray diffraction in the system H_2 - CH_4 - H_2O at a pressure of 20 MPa and 40 mol% of hydrogen content in the initial gas mixture. They concluded that hydrate formed is sI with cell parameter of 11.86 Å at 133 K [34]. Matsumoto *et al.* investigated H_2 - CH_4 hydrates prepared at various conditions were by PXRD and Raman spectroscopy to reveal hydrate structure, cage occupancies and mole fraction of H_2 and CH_4 . They noticed that H_2 - CH_4 binary hydrates can be either sI or sII depending on pressure, temperature, composition and formation time. More importantly, that they showed that in some cases sI can be formed first even before the thermodynamically stable sII and that these hydrates can be formed at more moderate conditions than pure H_2 or tuned H_2 -THF binary hydrates [35]. As hinted earlier, the presence of thermodynamic promoters in sII or sH improved the formation conditions significantly but on the expense of sharp decrease in storage capacity due to filling the large cages.

So, one way to improve the clathrate storage capacity for hydrogen is to allow both small and large cage occupancies by using small gas molecules such as CH₄ and CO₂. Belosludov *et al.* theoretically investigated the hydrogen storage in binary hydrogen-methane clathrate hydrates and showed that methane concentration of 6% stabilizes the cubic sI [36,37].

Grim *et al.*, using Raman spectroscopy and PXRD, showed that H₂ can be stored in both small and large cages of sI. They basically used pre-synthesized CH₄ and CO₂ sI clathrate as a “templates” for hydrogen clathrates. Although the storage potential was less than sII, they proved the concept that H₂ can occupy both small and large cages and multiple cage occupancy is feasible in case of sI. It should be noted that CH₄ and CO₂ sI clathrate were synthesized at 11 and 1.7 MPa, respectively. Accordingly, the CH₄ initial templates is almost fully occupied with $\Theta_s=0.96$ and $\Theta_l=0.99$, a value similar to CO₂ large cages $\Theta_l=0.98$ occupancy as calculated by CSMGem [3]. Consequently, there is a big chance that cages, especially large ones, accommodate hydrogen together with CH₄ or CO₂. Such a mixed occupation would greatly impact the estimated storage capacity of those clathrates.

Generally, the cage occupancy depends mainly on two important interrelated properties: (1) the stability of those (pre-)occupied cages and (2) the ability of guest gas to diffuse into those specific cages at first place. The latter is determining factor in transport phenomena and processes such as mass transfer depend on the inter-cages transition energy barrier. Calculating those barriers will enable us to accurate estimate parameters such as diffusion constant in intact hydrate phase and therefore give better understanding of practical issue such as the slow kinetics of hydrogen storage or CO₂/CH₄ replacement [38–41].

The diffusion mechanism suggested in the literature refers to that hydrogen diffuses most probably through hexagonal faces [42–44].

On the contrary, some other computational [45,46] and experimental [47,48] evidences strongly suggested that guest molecules can hop between all cages without significant overall changes to the hosting water network, despite that their nominal size exceeds the opening in the hexagonal or pentagonal face [49]. Peters *et al.* suggested that guest transport is supported by a water-hopping type mechanism to explain those contradictions. In such scenario the hydrogen bonds of a water molecule are completely dislocated and the hydrogen bond is broken while other bonds are elongated to keep the ring intact during transition [46]. Another study suggested the "help gas" mechanism in which an additional guest molecule enhance the diffusivity of the main guest by mutual interaction with the water network [50,51]. On the other hand, a direct transition mechanism for gas diffusion in gas hydrates was proposed based on density functional theory (DFT) calculations. This approach does not involve defects or helping gases. For instance, Alvi and Ripmeester [52] considered rigid cages to calculate the diffusion of H₂ in sII hydrates using B3LYP and MP2 levels of theory. They estimated that the H₂ guest needs 5–6 kcal/mol to diffuse through a hexagonal face of the large cage. That value increases about 5 or 6 times in case of pentagonal face . Other theoretical studies suggested that the cage-to-cage hopping of gas molecules through the five- and six-membered water rings involves distortion of the local water rings and requires no other structural defects within the hydrate framework [53,54]. However, the cage structures are partially constrained; therefore, these calculations may not be able to fully reveal the important factors related to the gas cage-to-cage hopping in gas hydrates [45].

To summarize, there are two extreme approaches try to resolve those contradiction between computational and experimental data (1) complete distortion of H-bonding network where the diffusion is facilitated by other molecule or crystal defect and (2) global structure flexibility that is enhanced by equitable sharing of the bond elongations. Thus, the proper understanding of inter-cage transport at the molecular level lies largely in the appropriate estimation of the flexible transitions.

This paper aims to study the cage occupancy and diffusion in single (H_2), mixed ($\text{CH}_4 - \text{H}_2$) and ($\text{CO}_2 - \text{H}_2$) sI clathrates. In addition, we will report the stability, binding energy, and optimum storage capacity of CH_4 and CO_2 in sI clathrate containing hydrogen. Finally, we will present all possible diffusion paths of hydrogen in sI empty and filled with frameworks. To evaluate the hydrogen bond network's ability to enhance global structure flexibility, we consider the diffusion through fully relaxed structures since the proper evaluation of diffusion is important to estimate the hydrogen storage in sI CH_4 or CO_2 clathrates.

2 Computational Methods

We performed here density functional theory (DFT) calculations [55] using projected augmented wave (PAW) pseudopotentials with kinetic energy cutoff for wave function and charge density of 55 and 440 Ry, respectively [56]. A self consistency convergence criterion of at least 1×10^{-8} was used and all structures were fully optimized using force convergence threshold of at least 10^{-4} Ry/a.u. All calculations have been performed using $2 \times 2 \times 2$ mesh except those for sII large unit cell where we used Γ point calculation only. Gas molecules

such as H₂, CH₄ and CO₂ are interacting with water frameworks by means of van der Waals forces and hydrogen bonding [3]. Moreover, it is not only the guest-host interaction but also the guest-guest and host-host interactions that affect hydrate formation and stability [57,58]. *Ab initio* DFT calculations via Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) functional [59] with revised exchange parametrization of Zhang and Yang (revPBE) has been applied self consistently [60]. The improved GGA functionals such as PBE and its revised versions revPBE and RPBE can give more accurate chemisorption energies than the PW91 and PBE functionals [60–63], however it fails to include vdW dispersion forces or hydrogen bonding [64,65]. To illustrate, Pétuya *et al.* argued that the semilocal PBE functional can still reproduce experimental structural properties obtained by neutron diffraction and estimate stability of clathrates even better than non-local vdw-DF [66]. In another study, Vlastic *et al.* pointed out that revPBE works very well for gas and THF hydrates and could accurately determine their mechanical and vibrational properties. They suggested that particularly revPBE provided a unique combination of accuracy and low computational cost, when compared to other XC functionals including those that take into account long-range van der Waals interactions [67]. On the other hand, Cao *et al.* [68] suggested that the improved nonlocal van der Waals density functional (vdw-DF2) with the inclusion of a long-range term of the correlation energy is necessary to account for intermolecular dispersion interactions [69]. Accounting for the importance of these forces, we have used both revPBE and vdw-DF2 as implemented in Quantum Espresso (QE) software [70], thus addressing the discrepancies in the literature sources. The thermodynamic stability and storage capacity of mixed (CH₄ - H₂, CO₂ - H₂) sI clathrates was evaluated using the cohesive energy (E_{coh}) and binding energy (E_b).

Cohesive energy (E_{coh}) per water molecules is calculated as [29]:

$$E_{coh} = \frac{E_{hydrate} - (x.E_{H_2} + y.E_{gas} + 46E_{H_2O})}{46}$$

The binding energy (E_b) is calculated as [71,72]:

$$E_b = E_{hydrate} - [E_{H_2} + E_{residual}]$$

where $E_{hydrate}$, E_{CO_2} , E_{gas} , E_{H_2O} , $E_{residual}$ are the energies of hydrate, hydrogen, gas (CO_2 or CH_4), water and the hydrate with one hydrogen molecule less. The minimum energy paths (MEP) between two minima were identified using NEB and CI-NEB methods with convergence criterion (< 0.05 eV/Å). Transition state structures were confirmed by presence of only one imaginary frequency along the reaction coordinate. Vibrational frequency calculation for those transition states were performed via DFPT (Density-Functional Perturbation Theory) calculations as implemented in QE package. [73].

3 Results and discussion

3.1 H_2 cage occupancy

The clathrate volumetric or gravimetric storage capacity depends on hydrate's stability and cage occupancy, while the diffusion rate of a gas molecule through the cages influences the storage kinetics. A major drawback of van der Waals and Platteeuw (vdW-P) theory is that it assumes single cage occupancy and ignores guest-guest interaction [74–76]. To overcome that, we used *ab initio* calculation of binding energy of gases in different cages to evaluate multiple cage occupancies and stability of hydrates. Calculating the binding energy in isolated cage models in order to evaluate occupancy in different cages has been proven to be a good compromise between high accuracy and computational

performance [77–79]. The small cage was modelled with a 20-molecule water cluster. In this structure, 8 oxygen molecules are organized in perfect cube (O_h) at a distance of 3.91 Å from the center of the cage while the remaining 12 oxygen are positioned at 3.95 Å from cage center. For the large cage, a 24-molecule model cluster is used where oxygen atoms are positioned in between 4.04 Å and 4.64 Å from the cage center. For most of the hydrogen atoms the O-H bond length is approximately 0.96 Å. Thus, the cluster models agree with the average x-ray structure of sI as well as the optimized crystal model [80,81] as shown in **Fig.1**.



Figure 1: Optimized geometries of empty (a) small (5^{12}) and (b) large ($5^{12}6^2$) cages of sI clathrate.

We calculated the binding energies as a function of the number of H_2 gas molecules bound to the sI individual cages using both vdW-DF2 and revPBE generalized gradient approximation (GGA). Here, the binding energy is defined as the energy difference between the cluster (host cage and guest molecule(s)) and the summation of system individual components. In case of n multiple gas occupancies, we subtract n time the energies of single gas molecule. For example, in case of H_2 occupancy in 5^{12} cage, we have calculated the encapsulation energy of 1, 2 and 3 hydrogen molecules while for $5^{12}6^2$ we considered encapsulation reactions with up to 6 H_2 molecules. For either low or high occupation of $n H_2@5^{12}$ and $nH_2@5^{12}6^2$, it has been noticed that the calculated

binding energies are not favouring the hydrogen encapsulation in both small and large sI clathrate cages even at low occupancies using revPBE as summarized in **Table 1**. This inconsistency with experimental evidences is not totally surprising because almost all popular PBE functionals are not able to describe vdW dispersive interactions which are dominant in the presence of non-polar gas molecules such as hydrogen [82, 83].

So, using vdW-DF2 we further examined the structure and stability of the

Table 1: **vdW-DF2 and revPBE binding energies (eV) for H₂ in sI**

Reaction	$\Delta E_0(\text{revPBE})$	$\Delta E_0(\text{vdW-DF2})$	$\Delta E_0 \text{ H}_2\text{-H}_2$ (vdW-DF2)
1H ₂ +S=1H ₂ @S	0.023	-0.123	-
2H ₂ +S=2H ₂ @S	0.258	-0.147	0.020
3H ₂ +S=3H ₂ @S	0.598	-0.070	0.062
1H ₂ +L=1H ₂ @L	0.005	-0.108	-
2H ₂ +L=2H ₂ @L	0.108	-0.216	-0.002
3H ₂ +L=3H ₂ @L	0.341	-0.210	0.013
4H ₂ +L=1H ₂ @L	0.546	-0.243	0.013
5H ₂ +L=2H ₂ @L	-	-0.225	0.037
6H ₂ +L=3H ₂ @L	-	-0.186	0.037

H₂O/H₂ models. For H₂@5¹² model, the calculation predicted that hydrogen molecule is off-centre by only 0.2 Å. However, this distance from cage center increased to 1.27 Å in case of 5¹²6² cage. This deviation from center in large cage can be explained by the presence of different cage faces (pentagonal and hexagonal) areas that have unequal interactions with the H₂ molecule. On the other hand, the equivalent 5¹² pentagonal faces have equal host-guest interactions areas that keep hydrogen molecule centred. For 2 H₂@5¹², the intermolecular distance in between the centres of mass is 2.92 Å while the distances from cage center are 1.32 and 1.46 Å. Likewise for 2H₂@5¹²6², this intermolecular distance

slightly increased to 3.03 Å and the two molecules stayed at remarkably equivalent distance of approximately 1.52 Å from cage center. When a third molecule is added to the small cage, the H₂ molecules are relaxed in an approximately equilateral triangle positions with intermolecular distances ranges from 2.59 to 2.64 Å and almost equal distances of average 1.51 Å from cage center. However, for 3 H₂@5¹²6², the hydrogen molecules preferred to position at isosceles triangle fashion with H₂-H₂ distances of 2.75, 2.74, and 3.21 Å. The mass centres of those three H₂ molecules are at a distance that ranges 1.67 and 1.77 Å from the large cage center. A combination of size effect and H₂-H₂ repulsions prevents the small cage to accommodate more than 3 H₂ molecules and the binding energy become positive. On the contrary, adding a fourth molecule to the large cage stabilized it at an optimum binding energy of -23.41 kJ/mol. While 2 of the 4 hydrogen molecules relaxed at cage off-center distance of 1.70 Å, the other couple maintained approximately 1.83 Å equal distances from the cage center. In that case, the H₂-H₂ distances are between 2.74 and 3.13 Å. The geometry optimization resulted in distorted tetrahedron of H₂ molecules with center-of-mass distances between 2.72 and 4.14 Å after adding a fifth hydrogen molecule. The off-center distance range increased to 1.42-2.28 Å, with the upper limit reflecting the increasing effect of H₂-H₂ repulsion. Finally, we examined 6 hydrogen molecules cluster, and similarly H₂-H₂ mass center distanced between 2.74-3.98 Å.

From **Table 1**, we can see that an increase in the number of H₂ molecules leads to an increase in binding energy per H₂ molecule and further stabilization of the cage due to the additional interaction of H₂ molecules. This is valid until the number of hydrogen molecules reaches an optimum cluster size above which additional hydrogen molecules destabilize the cage. Accordingly, it has

been found that 5^{12} cage can accommodate up to 2 H_2 molecules, while $5^{12}6^2$ had optimum cage occupancy of 4 H_2 molecules as shown in **Fig.2**. On the other hand, the inclusion of dispersive forces increased the stability structures in general and more specifically at higher hydrogen occupancies. For single H_2 occupancy, the differences between vdW-DF2 and revPBE is 14.12 and 10.08 kJ/mol for small and large cages, respectively. However, for the optimum occupancies, these numbers increased by 19-89% to reach 19.51 and 19.02 kJ/mol for small and large cages, respectively. In addition, our results using vdW-DF2 showed excellent agreement with those benchmark values calculated using higher level quantum chemistry methods. To illustrate, our calculated binding energies of single H_2 occupancy in small and large cages are -0.123 , -0.110 eV compared to -0.124 and -0.110 reported by Patchkovskii and Tse using second order Møller–Plesset (MP2) calculations, respectively [77]. To explain this



Figure 2: Optimized configurations of H_2 molecules at optimum cage occupancies inside (a) small (5^{12}) and (b) large cages ($5^{12}6^2$) of sI clathrate.

stabilization or destabilization, we should consider the relative weight of guest-guest interaction compared to host-guest interaction. To estimate the earlier we calculated the formation energies of a "bare" nH_2 cluster at the optimized geometry inside cages as shown in **Table 1**. Our calculations indicated that for lower cage occupancies up to the optimum, the H_2 - H_2 repulsion had a minor effect at both small and large cages and did not exceed 1.91 kJ/mol. How-

ever, increasing the number of H_2 molecule by only one H_2 molecule beyond that optimum resulted in H_2 - H_2 repulsion sharp increase by 3 times in case of small cage and about 2.8 time in case of large cage. In contrast, and at the same time, the attractive host-guest interactions between hydrogen and cage wall improved the cage stability to maximum at optimum occupancy. Adding further hydrogen molecules did not improve the stability as the contact area between hydrogen and cage wall has already reached the maximum at optimum occupancies. Thus, the H_2 - H_2 repulsion further dominated, as shown in **Fig.3**.

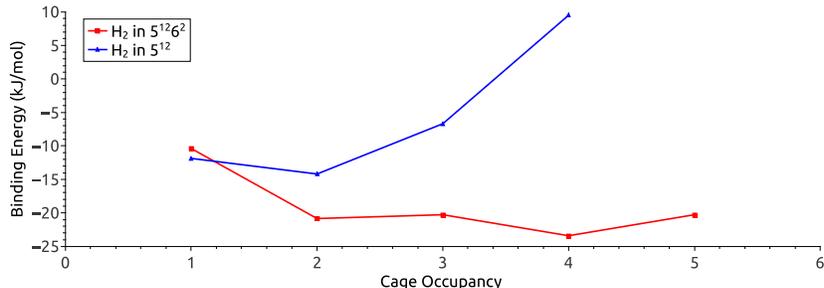


Figure 3: Binding energies as a function of the number of molecules for H_2 in small and large cages of sI clathrate.

3.2 (CH_4+H_2) and (CO_2+H_2) cage occupancy

Similar to H_2 , we studied the single occupancy of CO_2 , CH_4 , CH_4 - H_2 , and CO_2 - H_2 in individual cages. In all cases, we have found that the adsorption energy is dominated by van der Waals interactions in line with the above results. Unlike vdW-DF2, the absence of van der Waals forces in the GGA approximation showed that the inclusion of CO_2 and CH_4 in sI cage is not energetically favorable, contradicting experimental results as shown in **Table 2**.

Consequently, from hereafter, vdW-DF2 results will only be considered. The geometry relaxation for CH_4 and CO_2 @ 5^{12} cage showed that the gas tends to

Table 2: **Calculated interaction energy (eV) of CO₂ and CH₄.**

Guest Molecule	IE (revPBE)	IE (vdW) eV	IE (MP2) eV
1CH ₄ +S=1CH ₄ @S	0.021	-0.288	-0.337 [84]
1CO ₂ +S=1CO ₂ @S	0.235	-0.360	-0.390 [85]
1CH ₄ +L=1CH ₄ @L	0.089	-0.283	-0.295 [84]
1CO ₂ +L=1CO ₂ @L	0.063	-0.408	-0.417 [84]
2CO ₂ +L=2CO ₂ @L	0.101	-0.476	-
3CO ₂ +L=3CO ₂ @L	0.310	-0.160	-

stay at almost exactly the cage center. The single occupancy at the large cage shows some differences with the gas molecule relaxed off-centered by 0.21 and 0.52 Å for CH₄ and CO₂, respectively. Again, this small displacement is due to the unequal interactions with different faces of the large cage. One can conclude that for a single cage occupancy, the larger the molecules tend to position themselves at the cage center. More interestingly, comparing our binding energies results of single occupancy of CO₂ and CH₄ to those calculated by Atilhan *et al.* via the highly accurate MP2 method, an excellent agreement has been obtained as shown **Table 2** [84]. For CO₂@5¹² cage single, cage occupancy is slightly preferred than in case of CH₄ and the results are comparable to DF-MP2/AVTZ level of theory reported by Arismendi-Arrieta *et al.* [85]. Additionally, we calculated, for the first time to the best of our knowledge, the binding energies of double occupancy of (CH₄+H₂) and (CO₂+ H₂) in both small and large cage. The binding energy values indicated that inserting hydrogen destabilizes the small cage by 18.9 kJ/mol relative to CH₄ single occupancy. At the same time, H₂ will prefer to occupy an empty cage instead as shown in **Fig.4**. Similarly, trying to adsorb hydrogen molecule in a small cage pre-occupied by CO₂ destabilized the cage but to lesser extent. From energetic point of view , the

co-inclusion of ($\text{CO}_2 + \text{H}_2$) in small cage is more stable than the optimum H_2 double occupancy. On the other hand, the large cage showed flexibility to accommodate or store both molecules as detailed below. Additionally, the results showed that CO_2 occupancies in large cages is dominant over small cages. Finally, based on above results, one can conclude the separation efficiency in large cage is in the order of $\text{CO}_2 > \text{CH}_4 > \text{H}_2$ which perfectly agrees with previous experimental observations [86–88].

Except for the debatable tuning studies [89], hydrogen is generally stored in

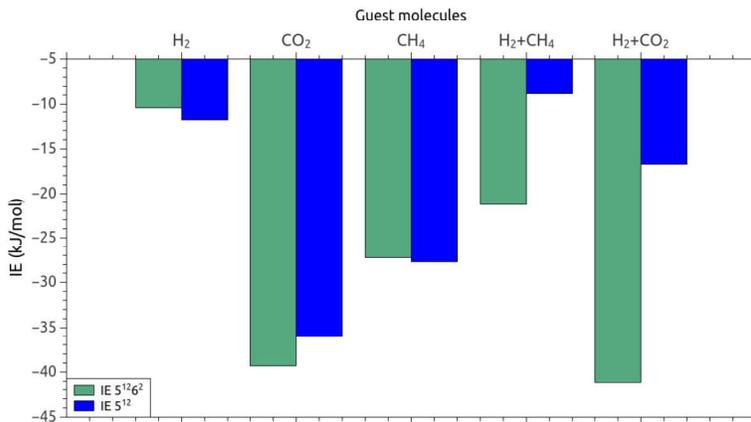


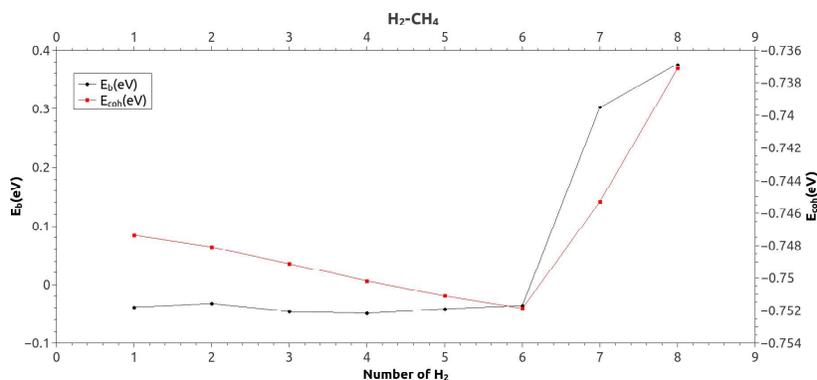
Figure 4: Binding energies as a function of the number of molecules for H_2 in small and large cages of sI clathrate.

the small cages of its binary clathrates such as H_2 -THF or H_2 -MTBE. One of the research targets of hydrogen clathrate is to store hydrogen in both small and large cages to get the full potential of clathrate storage capacity to meet DOE targets [90, 91]. Therefore, we examined the hydrogen accommodations in $5^{12}6^2$ cage being already occupied by a small gas molecule such as CH_4 or CO_2 . It was found that the H_2 inclusion in a large cage, already filled by CH_4 , will stabilize the cage by 21.23 kJ/mol which is better than single, double and triplet pure H_2 occupancies. However, it is still less than the optimum quadruple

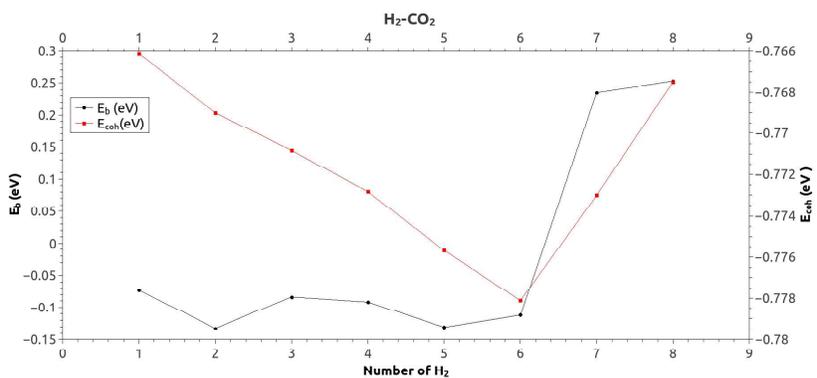
occupancy as detailed in **Table 1**. When the large cage is filled with a single CO₂ molecules, the inclusion of H₂ molecule will stabilize the cage significantly by -41.16 kJ/mol which is more stable than all possible pure hydrogen occupancies. Because the low binding energy of only -10.4 kJ/mole in case of pure hydrogen single cage occupancy at 5¹²6² cage, such heterogeneous occupancy (H₂+CO₂ or H₂+CH₄) binding energy results can better explain H₂ single cage occupancies in sI large cages proposed by experimental studies [35,92]. These results are in line with the concept that hydrate templates containing suitable energy gases can allow H₂ large cage occupancies, as shown in **Fig.4**.

3.3 *Thermodynamic and structural properties*

To further test the thermodynamic stability of the proposed mixed CH₄-H₂ occupancies in small and large cages, we evaluated the cohesive energy and binding energy when introducing H₂ to methane hydrate crystal structure. Assuming the cage is fully occupied by methane, we have found that the cohesive energy remains around -0.04 eV when filling the large cages. Similarly, the binding energy showed that introducing H₂ to the large cages increased the structure stability. However, trying to introduce a single hydrogen molecule to the small cages, the structure extremely destabilized, as indicated by both binding energy and cohesive energy values as shown in **Fig.5**. Similarly, the same behavior has been found when tried to introduce H₂ to CO₂ methane hydrate. These results confirm the outcome of isolated cage calculations. Accordingly, one can draw two conclusions. First, one is methane prefers to occupy the small cage. Second, it can be further stabilized in the large cage by a single hydrogen molecule. These multiple and mixed cage occupancies have implications on the energy storage capacity of sI methane clathrate containing hydrogen, as shown in **Fig.6**. Based on these results, we estimate that about 5.00 wt% of molec-



(a)



(b)

Figure 5: Binding and cohesive energy of (a) H_2-CH_4 and (b) H_2-CO_2 sI hydrates as function of hydrogen cage occupancy in large and small cages.

ular hydrogen can be stored in binary CH_4-H_2 sI, which meets the US DOE's 2020 4.5 wt% target. More importantly, the gravimetric and volumetric energy contents are 2.0 kW.h/kg and 1.8 kW.h/L, respectively. This higher energy density due to combining hydrogen with methane could even fulfill 2025 DOE targets of 1.7 kW.h/L. According to vdW-P theory [74,75], the empty hydrate is considered a metastable or hypothetical phase because the hydrate requires guest molecules to form a stable phase [93,94]. However, Falenty *et al.* showed that those metastable structures are experimentally accessible by removing all neon guests from sII clathrate using vacuum [95]. In another study, Krishnan *et*

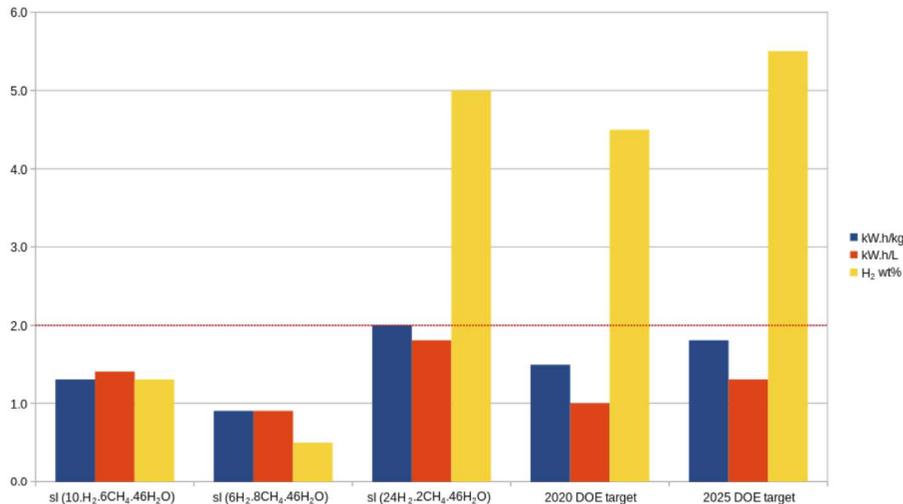


Figure 6: Energy density of possible binary H₂-CH₄ occupancies in sI clathrate compared to DOE targets.

al. evaluated the activation energy for release and uptake of neon to be 16.4 and 14.9 kJ/mol, respectively [96]. Thus, those empty cages can be considered as a valid starting point for our hydrate crystal calculations. We have calculated the optimized lattice parameters for the three common structures sI, sII, and sH considering both empty and fully occupied cages as shown in **Table 3**.

The small difference between lattice parameter of empty and filled cages for small gas guests agrees well with those reported in literature [97]. In case filled cages, we considered pure CH₄, CH₄-THF, and CH₄-Cyclooctane binary hydrates as representative examples for sI, sII and sH, respectively. In general, our results showed excellent agreement with experimental and computational data [3, 42, 80, 98]. The small deviation from experimental distances $d_{\text{O-H}}$ in case of sII and sH can be probably due to the difficulty of accurately determining H positions in X-ray experiments [81, 97]. Accordingly, the results indicate that vdW-DF2 can not only express the system energetics, but also it can give accurate structural properties.

Table 3: Calculated Lattice Parameters for sI, sII and sH of empty and filled crystal structures

Lattice Parameters		Empty		Filled			
		a [Å]	c [Å]	a [Å]	c [Å]	d _{O-H}	d _{o-o}
sI ¹	Calc.	12.03	-	11.98	-	0.99	2.79
	Exp.	12.00	-	12.00	-	0.97	2.76
sII ²	Calc.	17.33	-	17.33	-	0.99	2.79
	Exp.	17.35	-	17.35	-	0.81	2.77
sH ³	Calc.	12.43	10.16	12.47	10.16	0.99	2.79
	Exp.	12.33	9.92	12.33	9.92	0.78	2.78

¹ CH₄ for filled sI

² CH₄-THF for filled sII

³ CH₄-Cyclooctane for filled sH

3.4 H₂ diffusion in sI clathrate

Finally, we calculated the diffusion energy barriers of the cage to cage transfer for the H₂ in both empty and filled conditions. In addition to cage occupancy, diffusion of different guest molecules through hydrate cages is important determining factor for possible gas storage, extraction and separation [96, 99]. For example, in case of hydrogen storage, the practical application requires fast kinetics. Diffusion barriers depends on many factors but mainly on (1) gas molecules size (2) nature of gas molecule (2) cage(cavity) diameter (3) diffusion path (e.g via pentagonal or hexagonal face) and (4) cage occupancy. Through 12 images along the path from the center of one cage to another, we have calculated the diffusion barrier via nudged image elastic (NEB) followed climbing nudged image elastic band (cNEB) calculations. While the the first make sure that proper relaxation are perpendicular to the path, the later fine tune the result by allowing the image of highest energy to climb along the path regardless the effect of springs. It worth saying also that the accuracy of such energy barriers

are sensitive to proper relaxation of the host lattice at the first place [100,101]. To simplify, we will use AxB notation to refer to diffusion path where A and B to refer to initial and final state, respectively. The number x then will refer to the opening type (cage face) through which the gas diffuse. A or B can be small cage (S) and large cage (L) while x can either represent pentagon (5) or hexagon (6). While the diffusion path between large cages can be either via the pentagon L5L or the hexagon (L6L), the diffusion path between large and small cages has only one possibility (L5S) which is not symmetric due to the different sizes of small and large cage. In addition, as we highlighted earlier in **Table 1** and **Table 2**, the different gas molecules possess different binding energies in small and large cages. Thus, there are two different activation energies for L5S and S5L depending on the direction of diffusion path. **Fig.7** and **Table 4** summarize the energy profiles of all different diffusion paths of H_2 in both empty and filled cages. The flexibility of a cage can be estimated from

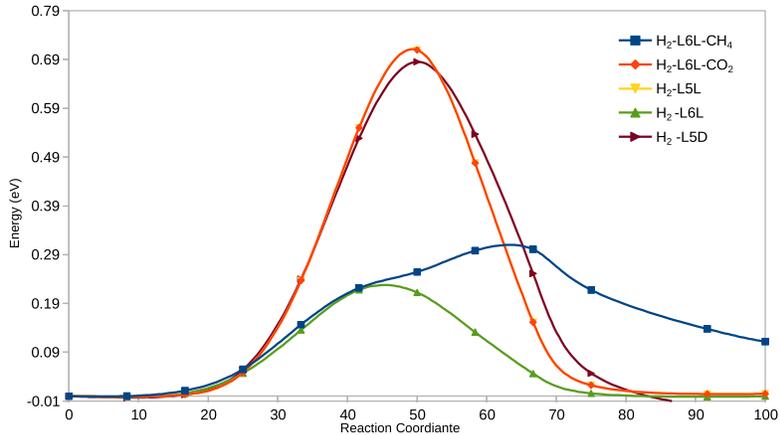


Figure 7: Diffusion Energy barriers of H_2 in different inter-cage transition systems (in eV) as a function of the relative progress along the reaction coordinate.

the deformation of its faces upon guest hopping. Inter-cage face deformations can account for the bonds' stretching and angular changes at a time and can be

directly estimated by calculating the area change of the cage face polygon defined by the oxygen atoms [54]. Those deformations and the area change values are summarized in **Fig.8** and **Table 4**. We found the L6L hydrogen hopping

Table 4: H₂ diffusion energy barriers and inter-cage deformation area of different transitions

System	Initial State	Final State	Ea(eV)	Ea(kJ/mol)	A(Å ²)*	ΔA%
LL	(H ₂)L5L	L5L(H ₂)	0.710	68.47	14.53	5.44%
	(H ₂)L6L	L6L(H ₂)	0.218	21.04	25.81	38.91%
	(H ₂)(CH ₄)L6L(CH ₄)	(CH ₄)L6L(CH ₄)(H ₂)	0.222	21.42	21.43	15.34%
	(H ₂)L6L(CH ₄)	L6L(CH ₄)(H ₂)	0.301	29.03	21.35	14.91%
	(H ₂)(CH ₄)L6L	(CH ₄)L6L(H ₂)	0.189	18.26	21.35	14.91%
	(H ₂)(CO ₂)L6L(CO ₂)	(CO ₂)L6L(CO ₂)(H ₂)	0.181	17.46	21.28	14.53%
	(H ₂)L6L(CO ₂)	L6L(CO ₂)(H ₂)	0.233	22.49	21.63	16.42%
	(H ₂)(CO ₂)L6L	(CO ₂)L6L(H ₂)	0.181	17.51	21.63	16.42%
LS	(H ₂)L5S	L5S(H ₂)	0.685	66.13	15.01	10.04%
	(H ₂)S5L	S5L(H ₂)	0.717	69.18	15.01	10.04%
	(H ₂)(CH ₄)L5S	(CH ₄)L5S(H ₂)	0.582	56.16	15.44	13.20%
	(H ₂)S5L(CH ₄)	S5L(CH ₄)(H ₂)	0.722	69.63	15.44	13.20%
	(H ₂)(CO ₂)L5S	(CO ₂)L5S(H ₂)	0.672	64.85	15.48	13.49%
	(H ₂)S5L(CO ₂)	S5L(CO ₂)(H ₂)	0.742	71.55	15.48	13.49%

*In empty cages the areas of small cage pentagonal face, large cage hexagonal and pentagonal (L5L) faces are 13.64, 18.58 and 13.78 Å², respectively

is in parallel to hexagonal cage face forming intermolecular hydrogen bonding between hydrogen molecule and the oxygen atoms building the cage as shown **Fig.8 (b)**. This temporal hydrogen bonding contributes to lower the activation energy barrier that was estimated to be 0.22 eV (21.04 kJ/mol) for a hydrogen molecule hopping between empty cages. The value is significantly lower than 27.02 kJ/mol reported using vdW-DF functional for sI large cage (5¹²6²) [42]. Moreover, it perfectly agrees with the similar (5¹²6⁴) L6L diffusion values of 22 kJ/mole value using AIMD calculation (B3LYP) and at the lower side of 21-25 kJ/mol range reported by using MP2 methods [52, 102]. We have also investigated the hydrogen diffusion when CO₂ or CH₄ occupies the large cage. Two important observations should be underlined: first, the presence of CO₂

or CH_4 in the cage facilitated the hydrogen hopping compared to empty cages, and second, the inter-cage deformation has been minimized, as shown in **Table 4**. Although there is no experimental values for H_2 diffusion in sI, it should be noted that being at lower side can be considered at the right direction as experimental activation energy barrier from NMR is only 0.03 eV (3 ± 1 kJ/mol) [103]. The large discrepancy between computational and experimental results are due to the fact that zero-point energy and quantum tunnelling are not considered which decreases the effective diffusion barrier [52] and cage occupancy are not considered [102]. These factors will be considered in our future study. Nevertheless, we considered our activation energy barrier at 0 K-for the scope of this study- is enough as it has already revealed important information and proved the concept. In absence of temporary guest-cage hydrogen bonding, hydrogen molecule diffusion via pentagonal face required to overcome 0.717 and 0.685 eV for L5L and L5S transitions which are slightly lower but agrees well with Li *et al.* and Roman-Perez *et al.* calculations using vdW-DF functional [42,97]. The higher energy barrier via pentagonal faces to/from the small cage is not sufficiently higher to underestimate its contribution to the overall diffusion. It is obvious that a lower barrier to diffuse via large cage hexagonal face channels dominates and enables faster kinetics for both adsorption and release. However, some hydrogen molecules should be retained in the small cage to get the full storage capacity of the clathrate structure. The latter can only happen through diffusion through pentagonal faces. Although those hops have relatively higher diffusion barriers, they are still affordable by the overall structure flexibility. The other challenge for optimum hydrogen storage is the ability to retain hydrogen in large cages. Based on above, the calculated 0.22 eV low barrier for hopping between large cages represent excellent opportunity for not only increasing the storage capacity but also the ease of hydrogen stor-

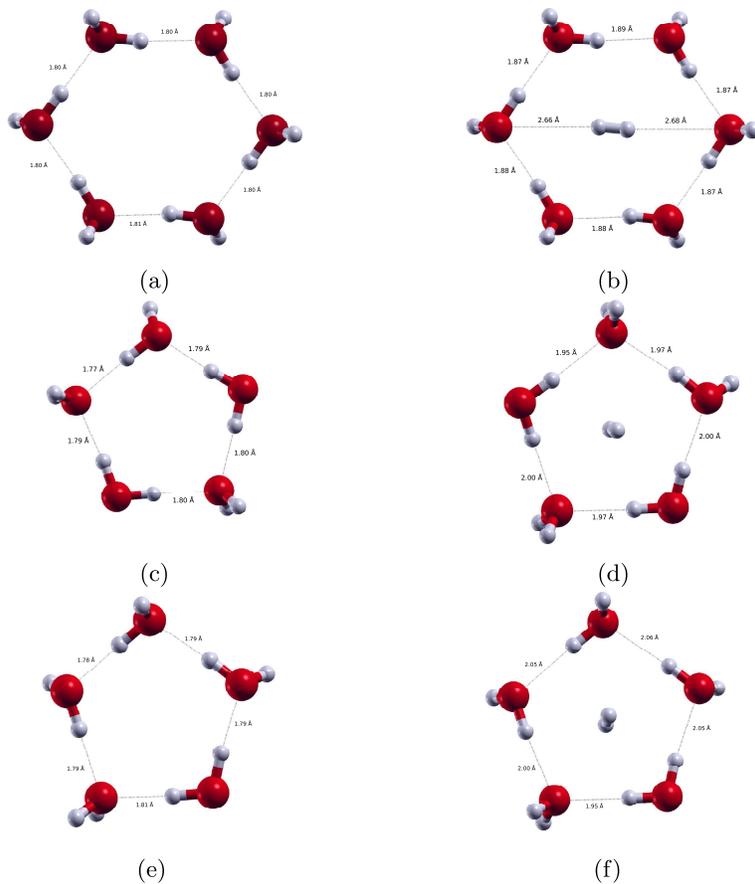


Figure 8: Representations of the transition state showing inter-cage face deformation during the H_2 diffusion.

age and extraction in clathrate as reported for sII [96, 99, 104]. However, our binding energy calculations showed also that even at the optimum occupancy of 4 H_2 molecules in $5^{12}6^2$ cage, the cage stability is still lower than those of CH_4 and CO_2 in large cages which supports to the 'template' concept discussed above. Several experimental pieces of evidence showed the presence of H_2 in the $5^{12}6^2$ cage of sI clathrate that have almost full large cage occupancy of CO_2 and CH_4 [35, 92]. So, these two contradicting effects leads us to think about the possibility of hydrogen diffusion to get heterogeneous $\text{H}_2\text{-CH}_4$ and $\text{H}_2\text{-CO}_2$

occupancy with in the same large cage, which may justify the experimental results. Although there are experimental and computational evidence for H_2 and

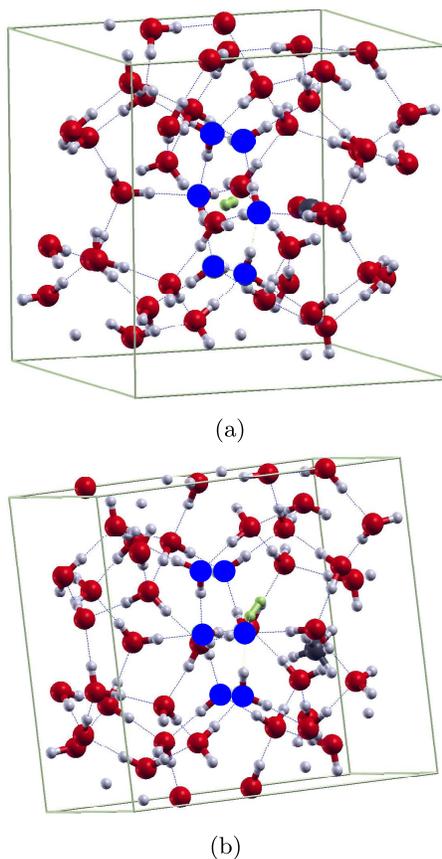


Figure 9: L6L system showing transition state of H_2 (green) passing through the hexagonal face (blue) from large cage filled with (a) $\text{H}_2\text{-CH}_4$ and (b) $\text{H}_2\text{-CO}_2$.

H-radical diffusion to occupied large cages of pure H_2 , binary $\text{H}_2\text{-THF}$ and $\text{H}_2\text{-C}_3\text{H}_8$ sII clathrates [78, 99, 105], the diatomic hydrogen diffusion between already sI occupied large cages -for the best of our knowledge- has not been reported yet. Our results showed that L6L hydrogen diffusion from the double occupied cage (DC) of (CH_4+H_2) to a large empty cage needs 18.26 kJ/mol compared 21.04 kJ/mol when hydrogen in a single occupied (SC) large cage diffuses to a neighbor empty large cage **Fig.9a**. However, when both large cages

are occupied by CH_4 , this diffusion required a slightly higher diffusion barrier of 21.42 kJ/mol. Yet, this is still feasible compared to the higher diffusion barriers required to diffuse through the pentagonal faces for both small and large cages. Similarly, hydrogen can diffuse from DC (CO_2+H_2) to empty or (CO_2)-filled large cage with energy barrier cost of 17.51 and 17.46 kJ/mol, respectively **Fig.9b**. In both case, the diffusion energy barrier is reduced significantly compared to the point of hydrogen hopping to empty large cage. Double occupation, either (CH_4+H_2) or (CO_2+H_2) did not only facilitate hydrogen diffusion into neighboring large cages, but also to empty small cages. To illustrate, the diffusion energy barriers from DC large cage of (CH_4+H_2) and (CO_2+H_2) into a small empty cage are 56.16 and 64.89 kJ/mol, respectively. Both values are also less than the 66.13 kJ/mol required for hydrogen to diffuse from SC large cage to empty small cage. Based on these results, one can anticipate that heterogeneous occupancies of (CH_4+H_2) and (CO_2+H_2) are energetically feasible and can compete with pure hydrogen occupancy in large cages. More importantly, this double occupation facilitate the hydrogen diffusion to neighboring small and large cages especially the empty ones. Consequently, the H_2 storage capacity can be enhanced. This lower diffusion barrier can be attributed to the fact that small molecules such as CH_4 or CO_2 (1) stabilize the cage and (2) alter the large cage dimensions during hydrogen diffusion. This can be noticed in the smaller inter-cage expansion area (ΔA) values required for hydrogen diffusion from DC large cage (CH_4+H_2 or CO_2+H_2) into other large cages as indicated in **Table 4**.

4 Conclusion

A comprehensive stability and diffusion study was performed to evaluate the viability of sI clathrate for hydrogen storage in the presence of CO_2 and CH_4 . The

computational data set pointed out that energy values obtained from generalized gradient approximation (GGA) functional, such as revPBE, can not properly evaluate the stability of gas clathrate. They are not reliable to determine the cage occupancy when compared to vdW-DF2 functional, providing results that are comparable to highly accurate wave function-based methods such as MP2 and the experimental values. Consequently, we used improved van der Waals density functional (vdW-DF2) to account for dispersion forces associated with adsorption of H₂, CH₄, and CO₂ in clathrates, focusing on sI. First, we analyzed the structural properties of the common hydrate phases of sI, sII and sH, in both empty and filled conditions, and the results agreed well with previous experimental and computational studies. Our calculations showed that: (1) the order of sI gas hydrate stability is CO₂ > CH₄ > H₂; (2) H₂ clathrate stability can be improved in H₂-CO₂ and H₂-CH₄ mixed systems with heterogeneous occupancy of different gases in the same cage; (3) multiple cage occupancies of H₂; and (4) the volumetric storage, gravimetric storage and molecular hydrogen content in H₂-CH₄ binary sI clathrate can reach 2.0 kW.h/kg and 1.8 kW.h/L and 5.0 wt% wt, respectively. Finally, the results proved that the direct transition mechanism is theoretically feasible through a fully relaxed structure. The presence of CO₂ or CH₄ facilitates the hydrogen diffusion to large and empty small cages by reducing the cage deformation. The estimated activation energy for hydrogen diffusion from doubly occupied (H₂-CH₄) to a large and a small cage are 0.189 and 0.582 eV, respectively. This set of computational results highlights the promising properties of sI clathrate for hydrogen storage and transportation, CH₄ recovery, and CSS in sI clathrates.

Acknowledgments

This work was performed on computing resources provided by CRIANN (Centre Régional Informatique et d'Applications Numériques de Normandie) Normandy,

France.

Funding

This work was supported by Industrial Chair ANR-TOTAL “NanocleanEnergy”.

References

- [1] Makagon Yuri F. *Hydrates of Hydrocarbons*. Pennwell Books, 1997.
- [2] Ioannis N. Tsimpanogiannis and Ioannis G. Economou. Monte Carlo simulation studies of clathrate hydrates: A review. *J. Supercrit. Fluids*, 134(December 2017):51–60, 2018.
- [3] E. Dendy Sloan and Carolyn Ann Koh. *Clathrate hydrates of natural gases, third edition*. CRC Press, third edition, 2007.
- [4] Yu A. Dyadin, I. S. Terekhova, T. V. Rodionova, and D. V. Soldatov. Half-century history of clathrate chemistry. *J. Struct. Chem.*, 40(5):645–653, 1999.
- [5] Xiangfang Li, Wen Yuan Liu, Shujie Liu, Jinqiu Hu, Yufeng Nan, Tian Tian, and Yunjian Zhou. A prevention and control method for natural gas hydrate in pipe strings during deepwater gas well production tests. *Nat. Gas Ind. B*, 7(1):82–92, 2020.
- [6] Elodie Gloesener, Özgür Karatekin, and Véronique Dehant. Stability and composition of CH₄-rich clathrate hydrates in the present martian subsurface, 2021.
- [7] Bertrand Chazallon, Jennifer A. Noble, and Arnaud Desmedt. Spectroscopy of Gas Hydrates: From Fundamental Aspects to Chemical En-

- gineering, Geophysical and Astrophysical Applications. *Gas Hydrates 1*, pages 63–112, 2017.
- [8] Sang Hyun Lee and Kyungtae Park. Conceptual design and economic analysis of a novel cogeneration desalination process using LNG based on clathrate hydrate, 2021.
- [9] Wonjung Choi, Woojin Go, Yohan Lee, Junghoon Mok, and Yongwon Seo. Mechanism and kinetics of guest exchange in sII hydrate – Flue gas replacement as revealed by experimental and computational approaches for hydrocarbon recovery and CO₂ sequestration. *Chem. Eng. J.*, (October):128119, 2020.
- [10] Gyeol Ko, Joonseop Lee, and Yongwon Seo. Separation efficiency and equilibrium recovery ratio of SF₆ in hydrate-based greenhouse gas separation. *Chem. Eng. J.*, 405(September 2020):126956, 2021.
- [11] Seokyeon Moon, Yunseok Lee, Dongju Seo, Seungin Lee, Sujin Hong, Yun-Ho Ahn, and Youngjune Park. Critical hydrogen concentration of hydrogen-natural gas blends in clathrate hydrates for blue hydrogen storage. *Renew. Sustain. Energy Rev.*, 141(September 2020):110789, 2021.
- [12] Mark Maslin, Matthew Owen, Simon Day, and David Long. Linking continental-slope failures and climate change: Testing the clathrate gun hypothesis. *Geology*, 32(1):53–56, 2004.
- [13] Timothy A. et al Minshull. Hydrate occurrence in Europe :A review of available evidence. *Mar. Pet. Geol.*, 111:2735–764, 2020.
- [14] Roy Andrew Partain and Constantinos Yiallourides. Hydrate occurrence in Europe: Risks, rewards, and legal frameworks, 2020.

- [15] Yun Ho Ahn, Seokyeon Moon, Dong Yeun Koh, Sujin Hong, Huen Lee, Jae W. Lee, and Youngjune Park. One-step formation of hydrogen clusters in clathrate hydrates stabilized via natural gas blending. *Energy Storage Mater.*, 24(March 2019):655–661, 2020.
- [16] Salvatore F. Cannone, Andrea Lanzini, and Massimo Santarelli. A Review on CO₂ Capture Technologies with Focus on CO₂-Enhanced Methane Recovery from Hydrates, 2021.
- [17] Seokyeon Moon, Sujin Hong, Yunseok Lee, Jae S. Lee, Yun Ho Ahn, and Youngjune Park. Enhancing Hydrogen Cluster Storage in Clathrate Hydrates via Defect-Mediated Lattice Engineering. *J. Phys. Chem. C*, 2021.
- [18] Jinfu Shu, Xiaojia Chen, I Ming Chou, Wenge Yang, Jingzhu Hu, Russell J Hemley, and Ho Kwang Mao. Structural stability of methane hydrate at high pressures. *Geosci. Front.*, 2(1):93–100, 2011.
- [19] M. V. Stackelberg and H. R. Müller. On the structure of gas hydrates. *J. Chem. Phys.*, 19(10):1319–1320, 1951.
- [20] Thomas C. W. Mak and Richard K. McMullan. Polyhedral Clathrate Hydrates. X. Structure of the Double Hydrate of Tetrahydrofuran and Hydrogen Sulfide. *J. Chem. Phys.*, 42(8):2732–2737, 1965.
- [21] Christopher I. Ratcliffe & Brian M. Powell John A. Ripmeester, John S. Tse. A new clathrate hydrate structure. *Nature*, 325:135–136, 1987.
- [22] Huen Lee, Jong Won Lee, Do Youn Kim, Jeasung Park, Yu Taek Seo, Huang Zeng, Igor L. Moudrakovski, Christopher I. Ratcliffe, and John A. Ripmeester. Tuning clathrate hydrates for hydrogen storage. *Mater. Sus-*

- tain. Energy A Collect. Peer-Reviewed Res. Rev. Artic. from Nat. Publ. Gr.*, 434(April):285–288, 2010.
- [23] J. A. Ripmeester and C. I. Ratcliffe. ^{129}Xe NMR studies of clathrate hydrates: New guests for structure II and structure H. *J. Phys. Chem.*, 94(25):8773–8776, 1990.
- [24] Aliakbar Hassanpouryouzband, Edris Joonaki, Mehrdad Vasheghani Farahani, Satoshi Takeya, Carolyn Ruppel, Jinhai Yang, Niall J. English, Judith M. Schicks, Katriona Edlmann, Hadi Mehrabian, Zachary M. Aman, and Bahman Tohidi. Gas hydrates in sustainable chemistry. *Chem. Soc. Rev.*, 2020.
- [25] Yuri A. Dyadin, Eduard G. Larionov, Andrei Yu Manakov, Fridrich V. Zhurko, Evgeny Ya Aladko, Tamara V. Mikina, and Vladislav Yu Komarov. Clathrate hydrates of hydrogen and neon. *Mendeleev Commun.*, 9(5):209–210, 1999.
- [26] Wendy L Mao, Ho kwang Mao, Alexander F. Goncharov, Viktor V. Struzhkin, Quanzhong Guo, Jingzhu Hu, Jinfu Hu, Russell J. Hemley, Maddury Somayazulu, and Yusheng Zhao. Hydrogen clusters in clathrate hydrate. *Science (80-.)*, 297(5590):2247–2249, 2002.
- [27] Wendy L. Mao and Ho Kwang Mao. Hydrogen storage in molecular compounds. *Proc. Natl. Acad. Sci. U. S. A.*, 101(3):708–710, 2004.
- [28] Niall J. English and Christian J. Burnham. Intra-cage structure, vibrations and tetrahedral-site hopping of H_2 and D_2 in doubly-occupied 51264 cages in sII clathrate hydrates from path-integral and classical molecular dynamics. *Appl. Sci.*, 11(1):1–9, 2021.

- [29] Jinxiang Liu, Jian Hou, Jiafang Xu, Haiying Liu, Gang Chen, and Jun Zhang. Ab initio study of the molecular hydrogen occupancy in pure H₂ and binary H₂-THF clathrate hydrates. *Int. J. Hydrogen Energy*, 42(27):17136–17143, 2017.
- [30] Ali Rasoolzadeh and Alireza Shariati. Hydrogen hydrate cage occupancy: A key parameter for hydrogen storage and transport. *Fluid Phase Equilib.*, 494:8–20, 2019.
- [31] Keisuke Katsumasa, Kenichiro Koga, and Hideki Tanaka. On the thermodynamic stability of hydrogen clathrate hydrates. *J. Chem. Phys.*, 127(4), 2007.
- [32] Alexandr Talyzin. Feasibility of H₂-THF-H₂ clathrate hydrates for hydrogen storage applications. *Int. J. Hydrogen Energy*, 33(1):111–115, 2008.
- [33] Takeshi Sugahara, Joanna C. Haag, Pinnelli S.R. Prasad, Ashleigh A. Warntjes, E. Dendy Sloan, Amadeu K. Sum, and Carolyn A. Koh. Increasing hydrogen storage capacity using tetrahydrofuran. *J. Am. Chem. Soc.*, 131(41):14616–14617, 2009.
- [34] Sergei S. Skiba, Eduard G. Larionov, Andrey Y. Manakov, Boris A. Kolesov, and Viktor I. Kosyakov. Investigation of hydrate formation in the system H₂-CH₄-H₂O at a pressure up to 250 MPa. *J. Phys. Chem. B*, 111(38):11214–11220, 2007.
- [35] Yuuki Matsumoto, R Gary Grim, Naveed M Khan, Takeshi Sugahara, Kazunari Ohgaki, E Dendy Sloan, Carolyn A Koh, and Amadeu K Sum. Investigating the thermodynamic stabilities of hydrogen and methane binary gas hydrates. *J. Phys. Chem. C*, 118(7):3581–3589, 2014.

- [36] Vladimir Belosludov, Ravil K Zhdanov, Maaouia Souissi, R V Belosludov, R K Zhdanov, O S Subbotin, H Mizuseki, M Souissi, Y Kawazoe, & V R Belosludov, and V R Belosludov. Theoretical modelling of phase diagrams of clathrate hydrates for hydrogen storage applications. *Molecular Simulation* Theoretical modelling of the phase diagrams of clathrate hydrates for hydrogen storage applications Theoretical modelling of the phase di. 2012.
- [37] R. V. Belosludov, R. K. Zhdanov, O. S. Subbotin, H. Mizuseki, Y. Kawazoe, and V. R. Belosludov. Theoretical study of hydrogen storage in binary hydrogen-methane clathrate hydrates. *J. Renew. Sustain. Energy*, 6(5), 2014.
- [38] Junghoon Mok, Wonjung Choi, and Yongwon Seo. Time-dependent observation of a cage-specific guest exchange in sI hydrates for CH₄ recovery and CO₂ sequestration. *Chem. Eng. J.*, 389(February):124434, 2020.
- [39] Geir Ersland, Jarle Husebø, Arne Graue, and Bjørn Kvamme. Transport and storage of CO₂ in natural gas hydrate reservoirs. *Energy Procedia*, 1(1):3477–3484, 2009.
- [40] Igor L Moudrakovski, Konstantin A Udachin, Saman Alavi, Christopher I Ratcliffe, and John A Ripmeester. Facilitating guest transport in clathrate hydrates by tuning guest-host interactions. *J. Chem. Phys.*, 142(7), 2015.
- [41] Ferdi Schüth. Technology: Hydrogen and hydrates. *Nature*, 434(7034):712–713, 2005.
- [42] Guillermo Román-Pérez, Mohammed Moaied, Jose M. Soler, and Felix Yndurain. Stability, adsorption, and diffusion of CH₄, CO₂, and H₂ in clathrate hydrates. *Phys. Rev. Lett.*, 105(14):8–11, 2010.

- [43] Qi Li, Brian Kolb, Guillermo Román-Pérez, José M Soler, Felix Yndurain, Lingzhu Kong, D C Langreth, and T Thonhauser. Ab initio energetics and kinetics study of H₂ and CH₄ in the SI clathrate hydrate. *Phys. Rev. B*, 84:153103, 2011.
- [44] Ángel Vidal-Vidal, Martín Pérez-Rodríguez, Jean Philippe Torré, and Manuel M. Piñeiro. DFT calculation of the potential energy landscape topology and Raman spectra of type I CH₄ and CO₂ hydrates. *Phys. Chem. Chem. Phys.*, 17(10):6963–6975, 2015.
- [45] Shuai Liang, Deqing Liang, Nengyou Wu, Lizhi Yi, and Gaowei Hu. Molecular Mechanisms of Gas Diffusion in CO₂ Hydrates. *J. Phys. Chem. C*, 120(30):16298–16304, 2016.
- [46] Baron Peters, Nils E.R. Zimmermann, Gregg T. Beckham, Jefferson W. Tester, and Bernhardt L. Trout. Path sampling calculation of methane diffusivity in natural gas hydrates from a water-vacancy assisted mechanism. *J. Am. Chem. Soc.*, 130(51):17342–17350, 2008.
- [47] A. N. Salamatin, A. Falenty, T. C. Hansen, and W. F. Kuhs. Guest Migration Revealed in CO₂ Clathrate Hydrates. *Energy and Fuels*, 29(9):5681–5691, 2015.
- [48] A. Falenty, A. N. Salamatin, and W. F. Kuhs. Kinetics of CO₂-hydrate formation from ice powders: Data summary and modeling extended to low temperatures. *J. Phys. Chem. C*, 117(16):8443–8457, 2013.
- [49] A. N. Salamatin, A. Falenty, and W. F. Kuhs. Diffusion Model for Gas Replacement in an Isostructural CH₄-CO₂ Hydrate System. *J. Phys. Chem. C*, 121(33):17603–17616, 2017.

- [50] Alondra Torres Trueba, Maaïke C. Kroon, Cor J. Peters, Igor L. Moudrakovski, Christopher I. Ratcliffe, Saman Alavi, and John A. Ripmeester. Inter-cage dynamics in structure I, II, and H fluoromethane hydrates as studied by NMR and molecular dynamics simulations. *J. Chem. Phys.*, 140(21), 2014.
- [51] Saman Alavi and John A. Ripmeester. Effect of small cage guests on hydrogen bonding of tetrahydrofuran in binary structure II clathrate hydrates. *J. Chem. Phys.*, 137(5), 2012.
- [52] Saman Alavi and John A. Ripmeester. Hydrogen-gas migration through clathrate hydrate cages. *Angew. Chemie - Int. Ed.*, 46(32):6102–6105, 2007.
- [53] Ángel M. Fernández-Fernández, Manuel M. Piñeiro, and Martín Pérez-Rodríguez. Computational simulation of fluorinated methane derivatives in type I clathrate hydrate. *J. Mol. Liq.*, 314, 2020.
- [54] Vidal-Vidal, M. Pérez-Rodríguez, and M. M. Piñeiro. Direct transition mechanism for molecular diffusion in gas hydrates. *RSC Adv.*, 6(3):1966–1972, 2016.
- [55] W. Kohn. Nobel lecture: Electronic structure of matter - Wave functions and density functional. *Rev. Mod. Phys.*, 71(5):1253–1266, 1999.
- [56] P. E. Blöchl. Projector augmented-wave method. *Phys. Rev. B*, 50(24):17953–17979, 1994.
- [57] Ravi Radhakrishnan and Bernhardt L. Trout. A new approach for studying nucleation phenomena using molecular simulations: Application to CO₂ hydrate clathrates. *J. Chem. Phys.*, 117(4):1786–1796, 2002.

- [58] Qiao Shi, Pinqiang Cao, Zhengde Han, Fulong Ning, Hao Gong, Yue Xin, Zhisen Zhang, and Jianyang Wu. Role of Guest Molecules in the Mechanical Properties of Clathrate Hydrates. *Cryst. Growth Des.*, 18(11):6729–6741, 2018.
- [59] John P. Perdew, Kieron Burke, and Matthias Ernzerhof. Generalized gradient approximation made simple. *Phys. Rev. Lett.*, 77(18):3865–3868, 1996.
- [60] Yingkai Zhang and Weitao Yang. Comment on “generalized gradient approximation made simple”, 1998.
- [61] B Hammer, L B Hansen, and J. K. Nørskov. Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals. *Phys. Rev. B - Condens. Matter Mater. Phys.*, 59(11):7413–7421, 1999.
- [62] B. Hammer and J.K. Nørskov. Theoretical Surface Science and Catalysis — Calculations and Concepts. *Adv. Catal.*, 45:71–129, 2000.
- [63] Ahmed Omran, Sun Hee Yoon, Murtaza Khan, Minhaj Ghouri, Anjaneyulu Chatla, and Nimir Elbashir. Mechanistic Insights for Dry Reforming of Methane on Cu/Ni Bimetallic Catalysts: DFT-Assisted Microkinetic Analysis for Coke Resistance. *Catalysts*, 10(9):1043, sep 2020.
- [64] Walter Kohn, Yigal Meir, and Dmitrii E. Makarov. Van der waals energies in density functional theory. *Phys. Rev. Lett.*, 80(19):4153–4156, 1998.
- [65] Tanja Van Mourik and Robert J. Gdanitz. A critical note on density functional theory studies on rare-gas dimers. *J. Chem. Phys.*, 116(22):9620–9623, 2002.

- [66] Claire Pétuya, Ludovic Martin-Gondre, Philippe Aurel, Françoise Damay, and Arnaud Desmedt. Unraveling the metastability of the SI and SII carbon monoxide hydrate with a combined DFT-neutron diffraction investigation. *J. Chem. Phys.*, 150(18), 2019.
- [67] Thomas M Vlastic, Phillip D Servio, and Alejandro D Rey. Infrared Spectra of Gas Hydrates from First-Principles. *J. Phys. Chem. B*, 123(4):936–947, 2019.
- [68] Xiaoxiao Cao, Yingying Huang, Xue Jiang, Yan Su, and Jijun Zhao. Phase diagram of water-methane by first-principles thermodynamics: Discovery of MH-IV and MH-V hydrates. *Phys. Chem. Chem. Phys.*, 19(24):15996–16002, 2017.
- [69] Kyuho Lee, Éamonn D. Murray, Lingzhu Kong, Bengt I. Lundqvist, and David C. Langreth. Higher-accuracy van der Waals density functional. *Phys. Rev. B - Condens. Matter Mater. Phys.*, 82(8):1–14, 2010.
- [70] Paolo Giannozzi, Stefano Baroni, Nicola Bonini, Matteo Calandra, Roberto Car, Carlo Cavazzoni, Davide Ceresoli, Guido L. Chiarotti, Matteo Cococcioni, Ismaila Dabo, Andrea Dal Corso, Stefano De Gironcoli, Stefano Fabris, Guido Fratesi, Ralph Gebauer, Uwe Gerstmann, Christos Gougoussis, Anton Kokalj, Michele Lazzeri, Layla Martin-Samos, Nicola Marzari, Francesco Mauri, Riccardo Mazzarello, Stefano Paolini, Alfredo Pasquarello, Lorenzo Paulatto, Carlo Sbraccia, Sandro Scandolo, Gabriele Sclauszero, Ari P. Seitsonen, Alexander Smogunov, Paolo Umari, and Renata M. Wentzcovitch. QUANTUM ESPRESSO: A modular and open-source software project for quantum simulations of materials. *J. Phys. Condens. Matter*, 21(39), 2009.

- [71] Ping Guo, Yi Long Qiu, Long Long Li, Qiang Luo, Jian Fei Zhao, and Yi Kun Pan. Density functional theory study of structural stability for gas hydrate. *Chinese Phys. B*, 27(4), 2018.
- [72] Stephen J. Cox, Michael D. Towler, Dario Alfè, and Angelos Michaelides. Benchmarking the performance of density functional theory and point charge force fields in their description of sI methane hydrate against diffusion Monte Carlo. *J. Chem. Phys.*, 140(17), 2014.
- [73] Stefano Baroni, Stefano de Gironcoli and Andrea Dal Corso. Phonons and related crystal properties from density-functional perturbation theory. *Rev. Mod. Phys.*, 73:515–561, 2001.
- [74] J H van der Waals and J C Platteeuw. Clathrate Solutions. *Adv. Chem. Phys.*, II:1–57, 1958.
- [75] J. C. Platteeuw and J. H. van der Waals. Thermodynamic properties of gas hydrates. *Mol. Phys.*, 1(1):91–96, 1958.
- [76] R. M. Barrer and W. I. Stuart. Non-stoichiometric clathrate compounds of water. *Proc. R. Soc. London. Ser. A. Math. Phys. Sci.*, pages 172–189, 1957.
- [77] Serguei Patchkovskii and John S. Tse. Thermodynamic stability of hydrogen clathrates. *Proc. Natl. Acad. Sci. U. S. A.*, 100(25):14645–14650, 2003.
- [78] Saman Alavi and John A. Ripmeester. Migration of hydrogen radicals through clathrate hydrate cages. *Chem. Phys. Lett.*, 479(4-6):234–237, 2009.

- [79] Niraj Thakre and Amiya K. Jana. Physical and molecular insights to Clathrate hydrate thermodynamics. *Renew. Sustain. Energy Rev.*, 135(September 2019):110150, 2021.
- [80] Konstantin A. Udachin, Christopher I. Ratcliffe, and John A. Ripmeester. Single crystal diffraction studies of structure I, II and H hydrates: Structure, cage occupancy and composition. *J. Supramol. Chem.*, 2(4-5):405–408, 2002.
- [81] Michael T. Kirchner, Roland Boese, W. Edward Billups, and Lewis R. Norman. Gas hydrate single-crystal structure analyses. *J. Am. Chem. Soc.*, 126(30):9407–9412, 2004.
- [82] Pattanasak Teeratchanan. First-principles studies of gas hydrates and clathrates under pressure. Technical report, 2017.
- [83] Xiaoxiao Cao, Yan Su, and Jijun Zhao. Stability and Vibrations of Guest Molecules in the Type II Clathrate Hydrate: A First-Principles Study of Solid Phase. *J. Phys. Chem. A*, 119(27):7063–7069, 2015.
- [84] Mert Atilhan, Nezih Pala, and Santiago Aparicio. A quantum chemistry study of natural gas hydrates. *J. Mol. Model.*, 20(4), 2014.
- [85] Daniel J. Arismendi-Arrieta, Álvaro Valdés, and Rita Prosimiti. A Systematic Protocol for Benchmarking Guest–Host Interactions by First-Principles Computations: Capturing CO₂ in Clathrate Hydrates. *Chem. - A Eur. J.*, 24(37):9353–9363, 2018.
- [86] Pinnelli S.R. Prasad and Burla Sai Kiran. Clathrate Hydrates of Greenhouse Gases in the Presence of Natural Amino Acids: Storage, Transportation and Separation Applications. *Sci. Rep.*, 8(1):1–10, 2018.

- [87] Junjie Zheng, Yean Kuan Lee, Ponnivalavan Babu, Peng Zhang, and Praveen Linga. Impact of fixed bed reactor orientation, liquid saturation, bed volume and temperature on the clathrate hydrate process for pre-combustion carbon capture. *J. Nat. Gas Sci. Eng.*, 35:1499–1510, 2016.
- [88] Zhiming Xia, Xiaosen Li, Zhaoyang Chen, Kefeng Yan, Chungang Xu, and Jing Cai. Hydrate-based hydrogen purification from simulated syngas with synergic additives. *Int. J. Hydrogen Energy*, 41(4):2649–2659, 2016.
- [89] Timothy A. Strobel, Craig J. Taylor, Keith C. Hester, Steven F. Dec, Carolyn A. Koh, Kelly T. Miller, and E. D. Sloan. Molecular hydrogen storage in binary THF-H₂ clathrate hydrates. *J. Phys. Chem. B*, 110(34):17121–17125, 2006.
- [90] Niall J. English and Christian J. Burnham. Intra-cage structure, vibrations and tetrahedral-site hopping of H₂ and D₂ in doubly-occupied 51264 cages in sII clathrate hydrates from path-integral and classical molecular dynamics, 2021.
- [91] Timothy A. Strobel, Keith C. Hester, Carolyn A. Koh, Amadeu K. Sum, and E. Dendy Sloan. Properties of the clathrates of hydrogen and developments in their applicability for hydrogen storage. *Chem. Phys. Lett.*, 478(4-6):97–109, 2009.
- [92] R. Gary Grim, Prasad B. Kerkar, Michele Shebowich, Melissa Arias, E. Dendy Sloan, Carolyn A. Koh, and Amadeu K. Sum. Synthesis and characterization of sI clathrate hydrates containing hydrogen. *J. Phys. Chem. C*, 116(34):18557–18563, 2012.
- [93] Fernando J.A.L. Cruz, Saman Alavi, and José P.B. Mota. Low-Temperature Thermodynamic Study of the Metastable Empty Clathrate

- Hydrates Using Molecular Simulations. *ACS Earth Sp. Chem.*, 3(5):789–799, 2019.
- [94] Fernando De Azevedo Medeiros, Iuri Soter Viana Segtovich, Frederico Wanderley Tavares, and Amadeu K. Sum. Sixty Years of the van der Waals and Platteeuw Model for Clathrate Hydrates - A Critical Review from Its Statistical Thermodynamic Basis to Its Extensions and Applications. *Chem. Rev.*, 120(24):13349–13381, 2020.
- [95] Andrzej Falenty, Thomas C. Hansen, and Werner F. Kuhs. Formation and properties of ice XVI obtained by emptying a type sII clathrate hydrate. *Nature*, 516(7530):231–233, 2014.
- [96] Yogeshwaran Krishnan, Mohammad Reza Ghaani, and Niall J. English. Electric-Field Control of Neon Uptake and Release to and from Clathrate Hydrates. *J. Phys. Chem. C*, 2019.
- [97] Qi Li, Brian Kolb, Guillermo Román-Pérez, José M. Soler, Felix Yndurain, Lingzhu Kong, D. C. Langreth, and T. Thonhauser. Ab initio energetics and kinetics study of H₂ and CH₄ in the SI clathrate hydrate. *Phys. Rev. B - Condens. Matter Mater. Phys.*, 84(15):2–5, 2011.
- [98] Konstantin A. Udachin, Christopher I. Ratcliffe, and John A. Ripmeester. Structure, composition, and thermal expansion of CO₂ hydrate from single crystal x-ray diffraction measurements. *J. Phys. Chem. B*, 105(19):4200–4204, 2001.
- [99] Niall English and Christian BURNHAM. Method and apparatus for controllable storage of hydrogen, 2020.

- [100] Graeme Henkelman and Hannes Jónsson. Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points. *J. Chem. Phys.*, 113(22):9978–9985, 2000.
- [101] Graeme Henkelman, Blas P. Uberuaga, and Hannes Jónsson. Climbing image nudged elastic band method for finding saddle points and minimum energy paths. *J. Chem. Phys.*, 113(22):9901–9904, 2000.
- [102] Thuat T. Trinh, Magnus H. Waage, Titus S. Van Erp, and Signe Kjelstrup. Low barriers for hydrogen diffusion in sII clathrate. *Phys. Chem. Chem. Phys.*, 17(21):13808–13812, 2015.
- [103] Takuo Okuchi, Igor L. Moudrakovski, and John A. Ripmeester. Efficient storage of hydrogen fuel into leaky cages of clathrate hydrate. *Appl. Phys. Lett.*, 91(17):2005–2008, 2007.
- [104] Yanhong Wang, Kaidong Yin, Shuanshi Fan, Xuemei Lang, Chi Yu, Shenglong Wang, and Song Li. The molecular insight into the “Zeolite-ice” as hydrogen storage material. *Energy*, 217:119406, 2021.
- [105] Sun Hwa Yeon, Jiwoong Seol, Youngjune Park, Dong Yeun Koh, Soo Kang Young, and Huen Lee. Spectroscopic observation of atomic hydrogen radicals entrapped in Icy hydrogen hydrate. *J. Am. Chem. Soc.*, 130(29):9208–9209, 2008.