Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supplementary Information

for

The Effect of H_2 Occupancy Modes in Small and Large Cages of s H_2-Tetrahydrofuran Hydrates on the Hydrates Stability and H_2 Storage Capacity

Ruyi Zheng [1, 2], Sohaib Mohammed [1], Yang Jia [1], Rituparna Hazra [1] and Greeshma Gadikota[1,*]

[1] School of Civil and Environmental Engineering, Cornell University, Ithaca, NY 14853

[2] Frontier Institute of Science and Technology, Xi'an Jiaotong University, Xi'an, Shaanxi 710054, China

*Corresponding author: Greeshma Gadikota, email: gg464@cornell.edu

Table S1. H_2 storage capacity in H_2 and H_2-THF hydrates

Hydrates	Storage capacity, wt%	P/MPa; T/K	Note (occupancy in small and large cages)	Reference
H_2	1-4	30-600; 150-300	Occupancy in small cages is around 1, it ranges from 1-4 in large cages, storage capacity increases with pressure; used MC simulation	(1)
H_2	1-6	150; 200-285	MD simulation of H_2 between slabs, saturated with H_2 gas; One H_2 occupancy in small cages, up to six H_2 in large cages	(2)
H_2	1-4	100-500; 170-273	MC simulation, one H_2 in small and up to four occupying large cages, dependent on pressure	(3)
H_2	2.6-3.3	-; 80-240	Based on MD simulation, most stable sII H_2 hydrates contain 2-3 H_2 in large cages and one H_2 molecule in small ones	(4)
D_2	4-5	0.1-200; 40-200	Neutron diffraction, single H_2 occupancy in small cages, double to quadruple occupancy in large once	(5)
H_2	1-5	15; 243	Experiments using PXRD and Raman, double H_2 in small and quadruple H_2 in large cages detected, but not uniform; H_2 hydrates formed by exchanging with N_2 hydrates	(6)
H_2	5.6	-	Ab initio simulation, the highest stability of H_2 is achieved by accommodating 2 and 5 H_2 in the small and large cages respectively	(7)
H_2	5.3	200-300; 249	Attributed two H_2 molecules in small cages and four H_2 in large cages using Raman	(8)
H_2	1-4	1-500; 200-300	MC simulation with fixed cage configuration; up to 1 H_2 in small, up to 4 H_2 in large cages;	(9)
H_2	5	200; 250	Thermodynamic model and ab initio simulation: the occupancy of H_2 in the small and large cages is 2 and 3.96	(10)
H_2	5-6	-	Highest stabilization energy of 5^{12}, $5^{12}6^2$ and $5^{12}6^4$ cages was obtained with H_2 occupancy of 2, 3, and 5 using DFT and ab initio calculation;	(11)
H_2	6.8	-; 250	Evaluated the storage capacity of small and large cages in a periodic unit cell of sI H_2 hydrates using first principle calculation; the lowest binding energy obtained by small and large cages occupied by two and four H_2 molecules, respectively	(12)
H_2-THF	1	5; 279.6	All large cages were occupied by THF; No evident of two H_2 occupying the small cages by NMR; Volumetric measurement suggested single occupancy of H_2 in small cages	(13)
H_2-THF	1.0	11.3; 280.8	Single occupancy of H_2 in small cages; all large cages were occupied by THF, with stoichiometric concentration of THF	(14)
H_2-THF	1	12.5-70, 20-270	Neutron diffraction, single occupancy of H_2 in small cages when THF occupied all large cages	(15)

H_2-THF	1-2	10-100; 100-250	MD simulation; single occupancy of H_2 in small cages; 2-3 H_2 occupying large cages when THF concentration is reduced, dependent on pressure	(16)
H_2-THF	-	-	H_2 is able to co-occupy the large cages with THF using DFT method	(17)
H_2, H_2-THF	4.0	12; 270	Occupancy of two H_2 in small cages; Interpreted H_2 occupancy using NMR; concluded the H_2 occupied large cages by reducing the THF concentration	(18)
H_2, H_2-THF	1.6-4.4	-; 140	Ab initio simulation; in pure H_2 hydrates, small cages may accommodate 1-2 H_2 and large cage may store 3-4; For H_2-THF hydrates, one H_2 in small cage, one THF+H_2 in large cage	(19)
H_2-THF	2.24	15-70; 243	Experimental exchanged N_2-THF hydrates with H_2, with P increased, occupancy of H_2 in small cage increased from 1 to 2; that in large cages ranges from 2 to 4; THF concentration 1 mol%	(20)
H_2-THF	1	74.3; 265	In-situ Raman; Detected H_2 occupying the large cages free from THF	(21)
H_2-THF	1.0	10-60; 270	NMR; Single occupancy of H_2 in small cages; large cages were occupied by THF, independent of THF concentration	(22)
H_2-THF	3.4	70; 255	Used powdered ice to prepare hydrates, storage capacity increased with reducing THF concentration from 1.0 to 3.4 wt%; Based on Raman spectra and XRD, multiple occupancy in large cages, single occupancy in small cages	(23,24)
H_2, H_2-THF	1-2	-	For pure H_2 hydrates, single occupancy in the small cage is more favorable, but with structure optimization, double occupancy is more favorable; for H_2-THF hydrates, no much difference for single or double occupancy	(25)

Table S2. Parameters of potential functions in the MD simulation

Molecules	Atom	Mass, g/mol	Charges, eV	*E*, kcal/mol	σ, Å	*l*, Å [a]
H_2O	H	1.008	0.5897	0	0	O-H: 0.9572 O-M: 0.1577
	O	15.9994	-	0.21084	3.1668	
	M	-	-1.1794	-	-	
H_2	H	1.00794	0.4932	0	0	H-H: 0.7414
	M_H	-	-0.9864	0.06816	3.0380	
THF	C_{f1}	12.011	0.024154	0.1094	3.816	C_{f1}-C_{f2}: 1.5439
	C_{f2}	12.011	0.024169	0.1094	3.816	C_{f2}-C_{f3}: 1.5309
	C_{f3}	12.011	0.171469	0.1094	3.816	C_{f1}-C_{f5}: 1.5309
	O_{f4}	15.999	-0.42513	0.17	3.367	O_{f4}-C_{f3}: 1.4197
	C_{f5}	12.011	0.171478	0.1094	3.816	O_{f4}-C_{f5}: 1.4197
	H_{f1-6}	1.008	0.005164	0.0157	2.974	C_{f1}-H_{f1-6}: 1.0863
	H_{f1-7}	1.008	-0.018458	0.0157	2.974	C_{f1}-H_{f1-7}: 1.0869
	H_{f2-8}	1.008	0.005161	0.0157	2.974	C_{f2}-H_{f2-8}: 1.0863
	H_{f2-9}	1.008	-0.018462	0.0157	2.974	C_{f2}-H_{f2-9}: 1.0869
	H_{f3-10}	1.008	0.022566	0.0157	2.974	C_{f3}-H_{f3-10}: 1.0858
	H_{f3-11}	1.008	0.007663	0.0157	2.974	C_{f3}-H_{f3-11}: 1.0954
	H_{f5-12}	1.008	0.022564	0.0157	2.974	C_{f5}-H_{f5-12}: 1.0858
	H_{f5-13}	1.008	0.007661	0.0157	2.974	C_{f5}-H_{f5-13}: 1.0954

[a] bond length

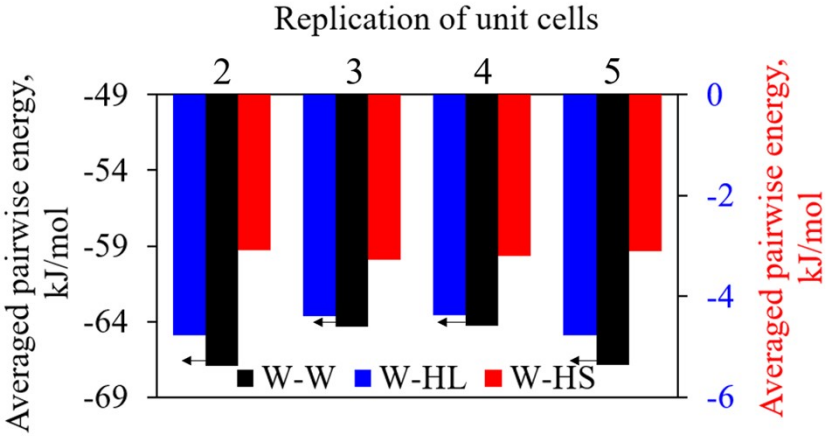

Figure S1. Pair-wise interaction energy between water (W), H_2 in the large cages (HL) and H_2 in the small cages (HS) with different replication of unit cells.

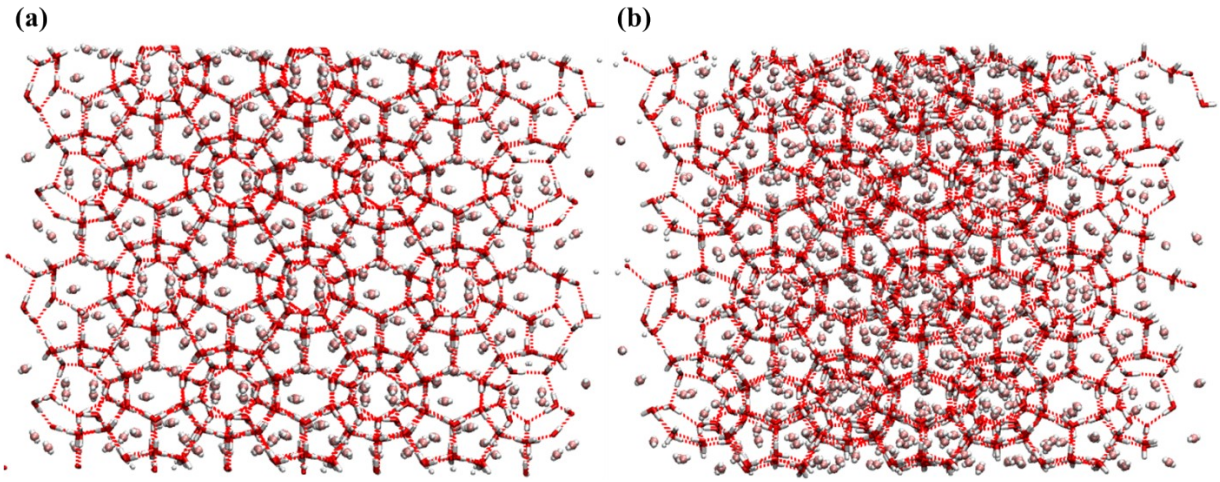

Figure S2. Simulation box of pure H_2 hydrates with 2×2×2 sII unit cells at (a) initial simulation time and (b) the end of simulation.

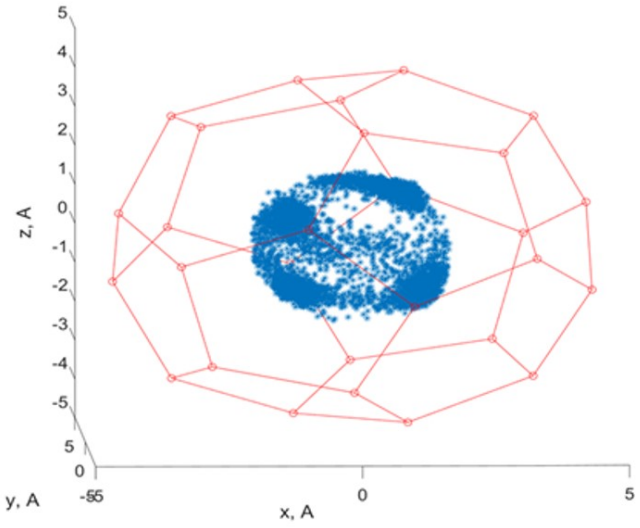

Figure S3. Distribution profile of the four H_2 molecules in one large cage (the origin of this coordinate represents the cage center).

The impact of H2 occupancy in the small cages on the motion of THF molecules is analyzed by comparing the rotational autocorrelation function (RACF), i.e., $C(t)$, as presented in Figure S3. It is found that the decay rate of THF orientation was fast, with an order of 10 ps. The RACF curves are fitted with the model described in Equation S1 to quantify the rotational relaxation time, with the parameters tabulated in **Table S3**. It is observed that the relaxation time of both oscillatory mode and rotational motion of THF increase when the small cages are occupied by 2 H_2 molecules.

$$C(t) = k \exp\frac{-t}{\tau_1} + (1-k)\exp\frac{-t}{\tau_2} \quad \text{(S1)}$$

where k is the pre-exponential constant; τ_1 and τ_2 are the relaxation time of oscillatory mode and rotational motion, ps.

Table S3. RACF parameters of THF with different occupancy modes in the small cages.

Configuration	Parameters		
	k	τ_1, ps	τ_2, ps
HS1-THF8	0.43	0.86	2.48
HS2-THF8	0.74	1.28	7.04

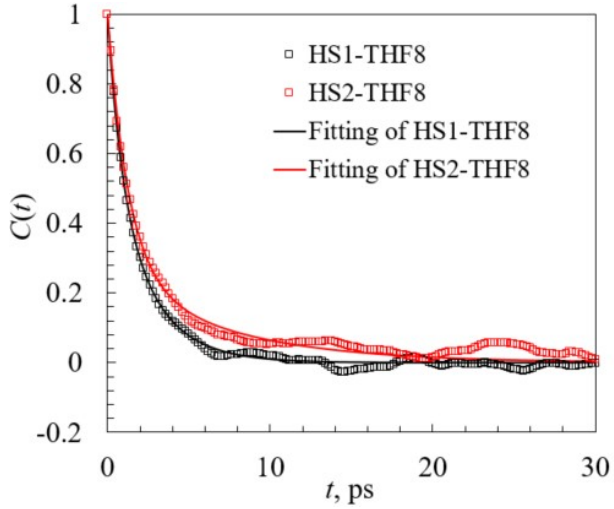

Figure S4. RACF curves of THF with different occupancy ratio of H_2 in the small cages.

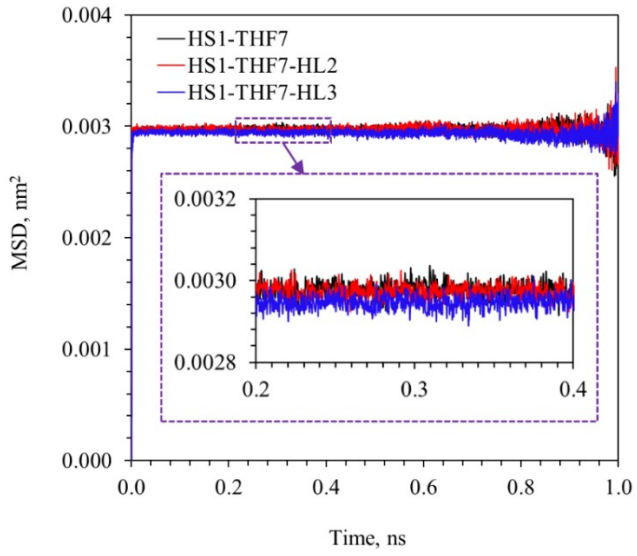

Figure S5. MSD of H_2O molecules with various occupancy modes of H_2 in the THF-free large cages.

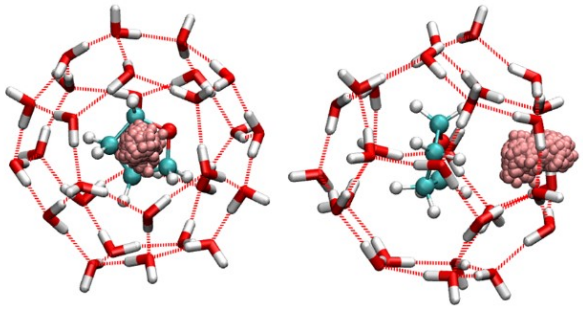

Figure S6. Distribution of one H_2 molecules in Configuration *HS1-(THF+HL)8-140K* from two perspectives.

Reference

1. Brumby PE, Yuhara D, Hasegawa T, Wu DT, Sum AK, Yasuoka K. Cage occupancies, lattice constants, and guest chemical potentials for structure II hydrogen clathrate hydrate from Gibbs ensemble Monte Carlo simulations. The Journal of Chemical Physics. 2019 Apr 7;150(13).
2. Frankcombe TJ, Kroes GJ. Molecular dynamics simulations of type-sII hydrogen clathrate hydrate close to equilibrium conditions. The Journal of Physical Chemistry C. 2007 Sep 6;111(35):13044-52.
3. Katsumasa K, Koga K, Tanaka H. On the thermodynamic stability of hydrogen clathrate hydrates. The Journal of Chemical Physics. 2007 Jul 28;127(4).
4. Krishnan Y, Ghaani MR, Desmedt A, English NJ. Hydrogen inter-cage hopping and cage occupancies inside hydrogen hydrate: Molecular-dynamics analysis. Applied Sciences. 2020 Dec 30;11(1):282.
5. Lokshin KA, Zhao Y, He D, Mao WL, Mao HK, Hemley RJ, Lobanov MV, Greenblatt M. Structure and dynamics of hydrogen molecules in the novel clathrate hydrate by high pressure neutron diffraction. Physical Review Letters. 2004 Sep 17;93(12):125503.

6. Lu H, Wang J, Liu C, Ratcliffe CI, Becker U, Kumar R, Ripmeester J. Multiple H_2 occupancy of cages of clathrate hydrate under mild conditions. Journal of the American Chemical Society. 2012 Jun 6;134(22):9160-2.
7. Ma R, Zhong H, Liu J, Zhong J, Yan Y, Zhang J, Xu J. Molecular insights into cage occupancy of hydrogen hydrate: A computational study. Processes. 2019 Oct 3;7(10):699.
8. Mao WL, Mao HK. Hydrogen storage in molecular compounds. Proceedings of the National Academy of Sciences. 2004 Jan 20;101(3):708-10.
9. Papadimitriou NI, Tsimpanogiannis IN, Economou IG, Stubos AK. The effect of lattice constant on the storage capacity of hydrogen hydrates: A Monte Carlo study. Molecular Physics. 2016 Sep 16;114(18):2664-71.
10. Patchkovskii S, Tse JS. Thermodynamic stability of hydrogen clathrates. Proceedings of the National Academy of Sciences. 2003 Dec 9;100(25):14645-50.
11. Tachikawa H, Iyama T, Kawabata H. Maximum capacity of the hydrogen storage in water clusters. Physics and Chemistry of Liquids. 2009 Feb 1;47(1):103-9.
12. Willow SY, Xantheas SS. Enhancement of hydrogen storage capacity in hydrate lattices. Chemical Physics Letters. 2012 Feb 16;525:13-8.
13. Florusse LJ, Peters CJ, Schoonman J, Hester KC, Koh CA, Dec SF, Marsh KN, Sloan ED. Stable low-pressure hydrogen clusters stored in a binary clathrate hydrate. Science. 2004 Oct 15;306(5695):469-71.
14. Hashimoto S, Murayama S, Sugahara T, Sato H, Ohgaki K. Thermodynamic and Raman spectroscopic studies on H_2 + tetrahydrofuran + water and H_2 + tetra-n-butyl ammonium bromide + water mixtures containing gas hydrates. Chemical Engineering Science. 2006 Dec 1;61(24):7884-8.

15. Hester KC, Strobel TA, Sloan ED, Koh CA, Huq A, Schultz AJ. Molecular hydrogen occupancy in binary THF − H_2 clathrate hydrates by high resolution neutron diffraction. The Journal of Physical Chemistry B. 2006 Jul 27;110(29):14024-7.
16. Kang DW, Lee W, Ahn YH, Lee JW. Exploring tuning phenomena of THF − H_2 hydrates via molecular dynamics simulations. Journal of Molecular Liquids. 2022 Mar 1;349:118490.
17. Kaur SP, Ramachandran CN. Hydrogen-tetrahydrofuran mixed hydrates: A computational study. International Journal of Hydrogen Energy. 2018 Oct 18;43(42):19559-66.
18. Lee H, Lee JW, Kim DY, Park J, Seo YT, Zeng H, Moudrakovski IL, Ratcliffe CI, Ripmeester JA. Tuning clathrate hydrates for hydrogen storage. Nature. 2005 Apr 7;434(7034):743-6.
19. Liu J, Hou J, Xu J, Liu H, Chen G, Zhang J. Ab initio study of the molecular hydrogen occupancy in pure H2 and binary H2-THF clathrate hydrates. International Journal of Hydrogen Energy. 2017 Jul 6;42(27):17136-43.
20. Park S, Koh DY, Kang H, Lee JW, Lee H. Effect of molecular nitrogen on multiple hydrogen occupancy in clathrate hydrates. The Journal of Physical Chemistry C. 2014 Sep 4;118(35):20203-8.
21. Nishikawa A, Tanabe T, Kitamura K, Matsumoto Y, Ohgaki K, Sugahara T. In situ Raman spectra of hydrogen in large cages of hydrogen+ tetrahydrofuran mixed hydrates. Chemical Engineering Science. 2013 Sep 20;101:1-4.
22. Strobel TA, Taylor CJ, Hester KC, Dec SF, Koh CA, Miller KT, Sloan ED. Molecular hydrogen storage in binary THF − H_2 clathrate hydrates. The Journal of Physical Chemistry B. 2006 Aug 31;110(34):17121-5.

23. Sugahara T, Haag JC, Prasad PS, Warntjes AA, Sloan ED, Sum AK, Koh CA. Increasing hydrogen storage capacity using tetrahydrofuran. Journal of the American Chemical Society. 2009 Oct 21;131(41):14616-7.
24. Sugahara T, Haag JC, Warntjes AA, Prasad PS, Sloan ED, Koh CA, Sum AK. Large-cage occupancies of hydrogen in binary clathrate hydrates dependent on pressures and guest concentrations. The Journal of Physical Chemistry C. 2010 Sep 9;114(35):15218-22.
25. Yedlapalli P, Lee S, Lee JW. Stable occupancy of hydrogen molecules in H_2 clathrate hydrates and H_2 + THF clathrate hydrates determined by ab initio calculations. Journal of Thermodynamics. 2010;2010(1):651819.