Hydrogen storage. (II) Hydrogen hydrates and hydrogen clathrates of ammonia borane.

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Outline

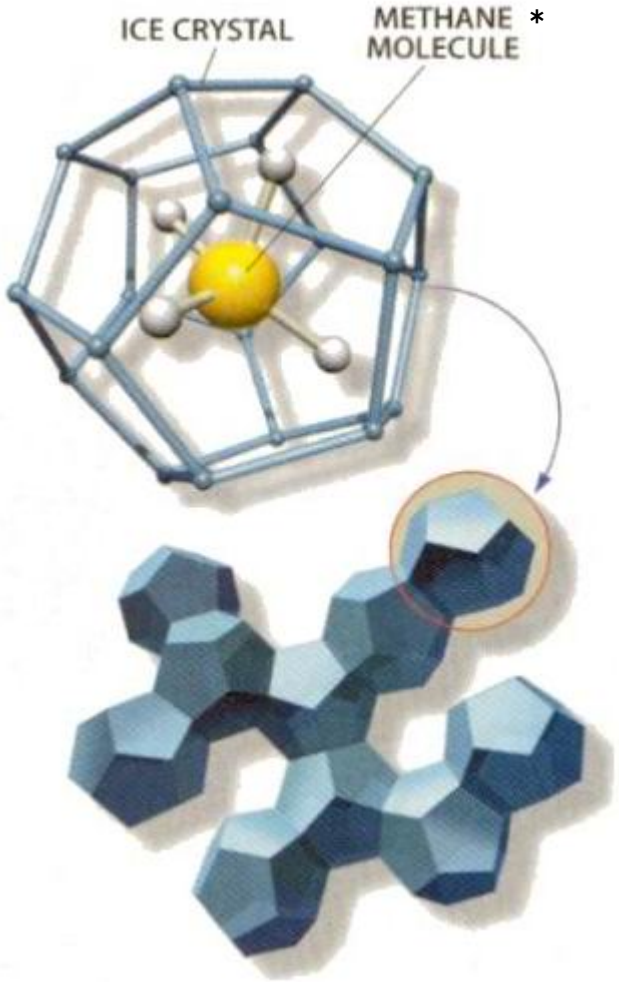
- Gas hydrates and hydrogen hydrates
- Hierarchical hydrogen storage
- Ammonia borane as a host molecule
- Design of AB clathrates. Formulation of the problem
- Host-host and host-guest interactions
- Possible cages of AB clathrates
- Possible periodic structures of AB clathrates
- Hydrogen capacity of AB clathrates
- The CCH structure and AB molecular crystal
- Van der Waals and Platteeuw model and hydrogen hydrates
- PT stability of clathrates and weak intermolecular interactions
- Applications of the statistical model

Gas hydrates

- Physical combination of water and gas molecules
- High pressure, low temperature (may be above 0ºC), and presence of guests stabilize the cages
- At 30 atm methane hydrates are stable at 0ºC, at 100 atm they are stable at 15ºC
- Three common structures and five types of the cages
- Not all cages are required to be filled (non-stochiometric compounds)

Cages per unit cell in different structures

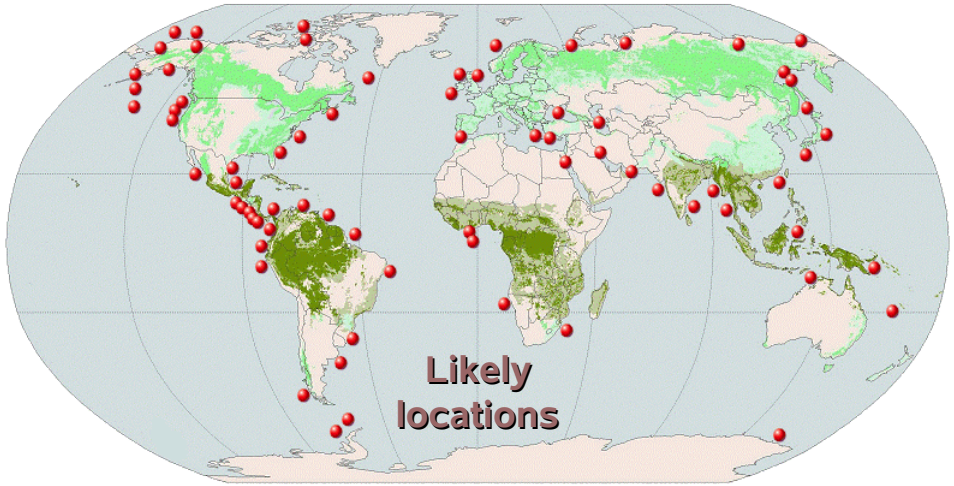
Cages	Structures		
	S-I	S-II	S-H
5^{12}	2	16	3
$5^{12}6^{2}$	6	-	-
$5^{12}6^{4}$	-	8	-
$4^{3}5^{6}6^{3}$	-	-	2
$5^{12}6^{8}$	-	-	1



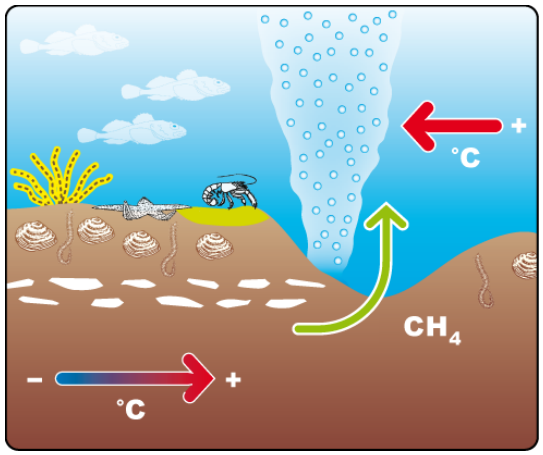
*www.rcom.marum.de/English/Structure_and_stability.html; www.hydratetech.com/hydrates.htm

Gas hydrates

- Large amount around the globe (in permafrost regions and marine sediments)
- Potential energy source which is twice as big as all other fossil fuels



- Potential *poison* in terms of global warming as methane (very strong greenhouse gas) is released upon heating
- Potential *remedy* in terms of global warming as CO_2 hydrates are heavier than water and can be stored on a sea bed

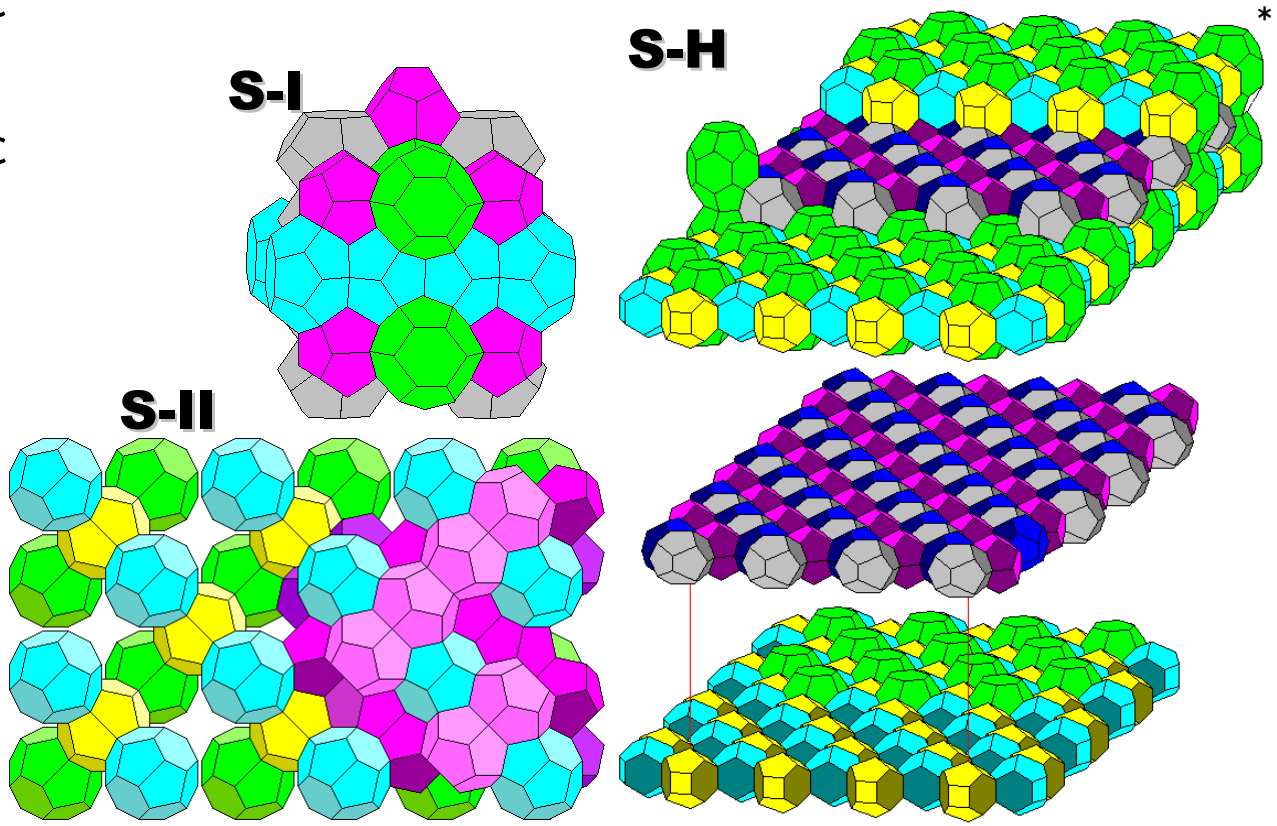


*http://cas.bellarmine.edu/tietjen/Environmental/Global%20Warming.htm; www.uni-kiel.de/future-ocean/a2/index.shtml

Gas hydrates

- S-I is formed from small guests (CH_4, CO_2). S-II is formed from intermediate sized compounds (C_3H_8, C_4H_{10}, nH_2). S-H requires large molecules along with small ones
- S-I is body-centered cubic $(SG)_2(LG)_6 46H_2O$[1]
- S-II is face-centered cubic $(SG)_{16}(LG+)_8 136H_2O$[1]
- S-H is hexagonal $(SG)_5(LG++)34H_2O$[1]

	S-I	S-II	S-H
5^{12}	2	16	3
$5^{12}6^2$	6	-	-
$5^{12}6^4$	-	8	-
$4^3 5^6 6^3$	-	-	2
$5^{12}6^8$	-	-	1



[1] SG – Small Guest, 1.8-2.2Å (Ar, O_2, N_2); LG – Large Guest, 1.8-2.7Å (C_2H_6); LG+ – 2.8-3.1Å (C_3H_8, $(CH_3)_3CH$); LG++ – 3.5-4.3Å ($(CH_3)_3CC_2H_5$)

*www.rcom.marum.de/English/Structure_and_stability.html; http://www.uwgb.edu/dutchs/PETROLGY/Clathrate-0.HTM

Gas hydrates

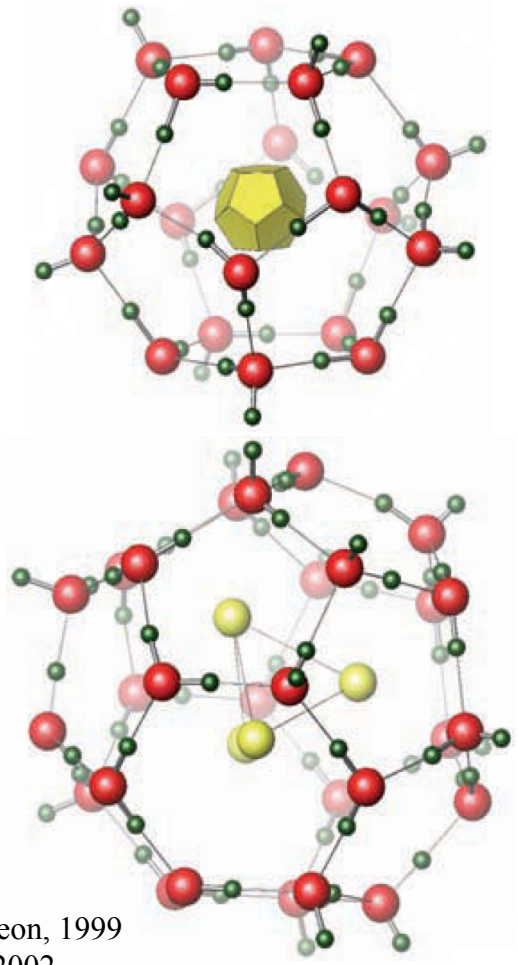
Characteristic*	I		II		H		
	Small	Large	Small	Large	Small	Medium	Large
Specification	5^{12}	$5^{12}6^2$	5^{12}	$5^{12}6^4$	5^{12}	$4^35^66^3$	$5^{12}6^8$
Coordination number (H_2O per cage)	20	24	20	28	20	20	36
Cages per unit cell	2	6	16	8	3	2	1
Mean cage radius, Å	3.95	4.33	3.91	4.73	3.94	4.04	5.79
Guest radius†, Å	1.8-2.2	1.8-2.7	1.8-2.2	2.8-3.1	1.8-2.2	1.8	3.5-4.3
Some guests	Ar, CO_2, N_2, CH_4	CO_2, C_2H_6	Ar, O_2, N_2, CH_4	C_3H_8, $(CH_3)_3$·CH	Ar, O_2, N_2, CH_4	CH_4	$(CH_3)_3$·CC_2H_5, C_6H_{12}
Lattice	Body-centred cubic		Face-centred cubic		Hexagonal		
Space group	Pm3n		Fd3m		P6/mmm		
Unit cell‡, Å	a = 12.03		a = 17.31		a = 12.26, c = 10.17		
Theoretical unit cell formula†	$(S)_2(L)_646H_2O$, S: small guest, L: large guest		$(S)_{16}(L+)_8136H_2O$, S: small guest, L+: larger guest		$(S)_5(L++)34H_2O$, S: small guest, L++: largest guest		
H_2O per unit cell	46		136		34		

Sloan, E. D. and Koh, C. A. Clathrate Hydrates of Natural Gases. CRC Press, 3rd edition, (2008)

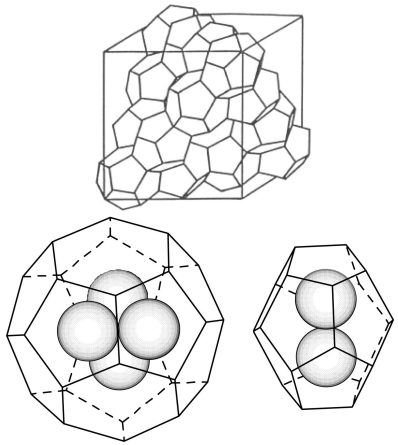
Hydrogen hydrates

- Were discovered in 1999[1]
- Stable under extreme conditions (2000 bar and 250 K)[2,3]
- Form structure II of gas hydrates[2,3]
- H_2/H_2O ratio can be as high as 1/2[2,3]
- Large cage holds up to 4 H_2 and small cage holds up to 2 H_2[2,3]
- Capacity of 1 H_2 per small cage was also reported[4]
- Maximum hydrogen content 5 wt%

Cages occupancies[4]



Cages occupancies[2]



Number of cages per unit cell

$8(5^{12}6^4) + 16(5^{12})$

Unit cell formula

$(4H_2)_8(2H_2)_{16}136H_2O$

Free cavity diameter[2]

Big cage: 6.67 Å

Small cage: 5.02 Å

H_2 diameter[2]: 2.72 Å

It is reported[4] that 20 different orientations of 1 H_2 molecule in the small cage are possible

[1] Dyadin et al., Clathrate Hydrates of Hydrogen and Neon, 1999
[2] Mao et al., Hydrogen Clusters in Clathrate Hydrate, 2002
[3] Patchkovskii and Tse, Thermodynamic stability of hydrogen clathrates, 2003
[4] Lokshin and Zhao, Storing Hydrogen in Crystalline Molecular Cages of Water, 2006

Hydrogen hydrates

- Pure hydrogen hydrates, up to 5 wt% of hydrogen, are stable under extreme conditions (2000 bar and 250 K)
- Several technics[1] to mitigate severity
  - Ternary Hydrogen Hydrates: a promoter molecule, tetrahydrofuran (THF), was found to reduce the formation pressure by a factor of 30 (from 2000 to 70 bar at 280 K). H_2 density is reduced down to 1 wt%
  - Semiclathrates: molecules with hydrogen-bonding abilities (e.g. tetra-n-butylammonium bromide, TBAB) can be involved into the water molecules network and form a complex composite which is stable at atmospheric pressure. H_2 density is reduced down to 0.2 wt%

[1] Struzhkin et al., Hydrogen Storage in Molecular Clathrates, 2007

Homework

For hydrates formed from three different gases

- Mostly methane (CH_4)
- Mostly ethane (C_2H_6)
- Mostly propane (C_3H_8)

hydration numbers (number of water molecules over number of gas molecules) were found to be

- 6.00
- 7.67
- 17.00

Using information giving in the summary table on hydrates confirm that methane and ethane form the structure I and propane forms the structure II of hydrates.

Hierarchical hydrogen storage

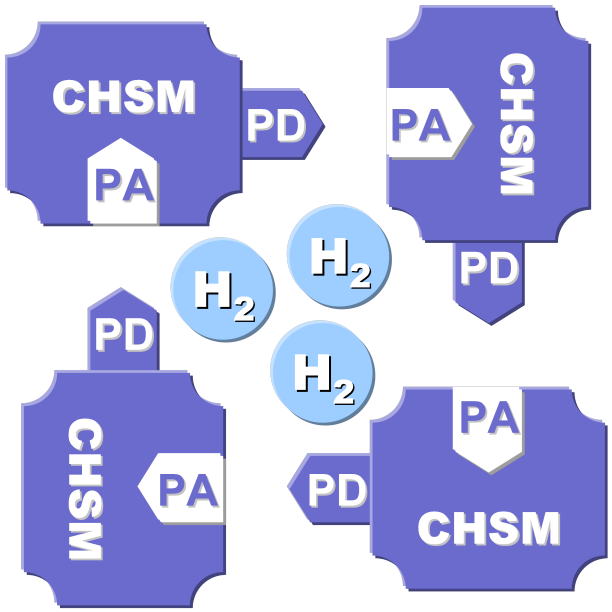
Hydrogen density

Compression	Liquefaction	Physisorption	Chemisorption	Chemical compounds
200-700 bar	20 K	Large surface area materials: MOFs; carbon based materials	Metal hydrides: $LiAlH_4$; $NaBH_4$; $Al(BH_4)_3$	NH_3; $Mg(NH_3)_6Cl_2$; NH_3BH_3

Hydrogen accessibility

Hierarchical hydrogen storage

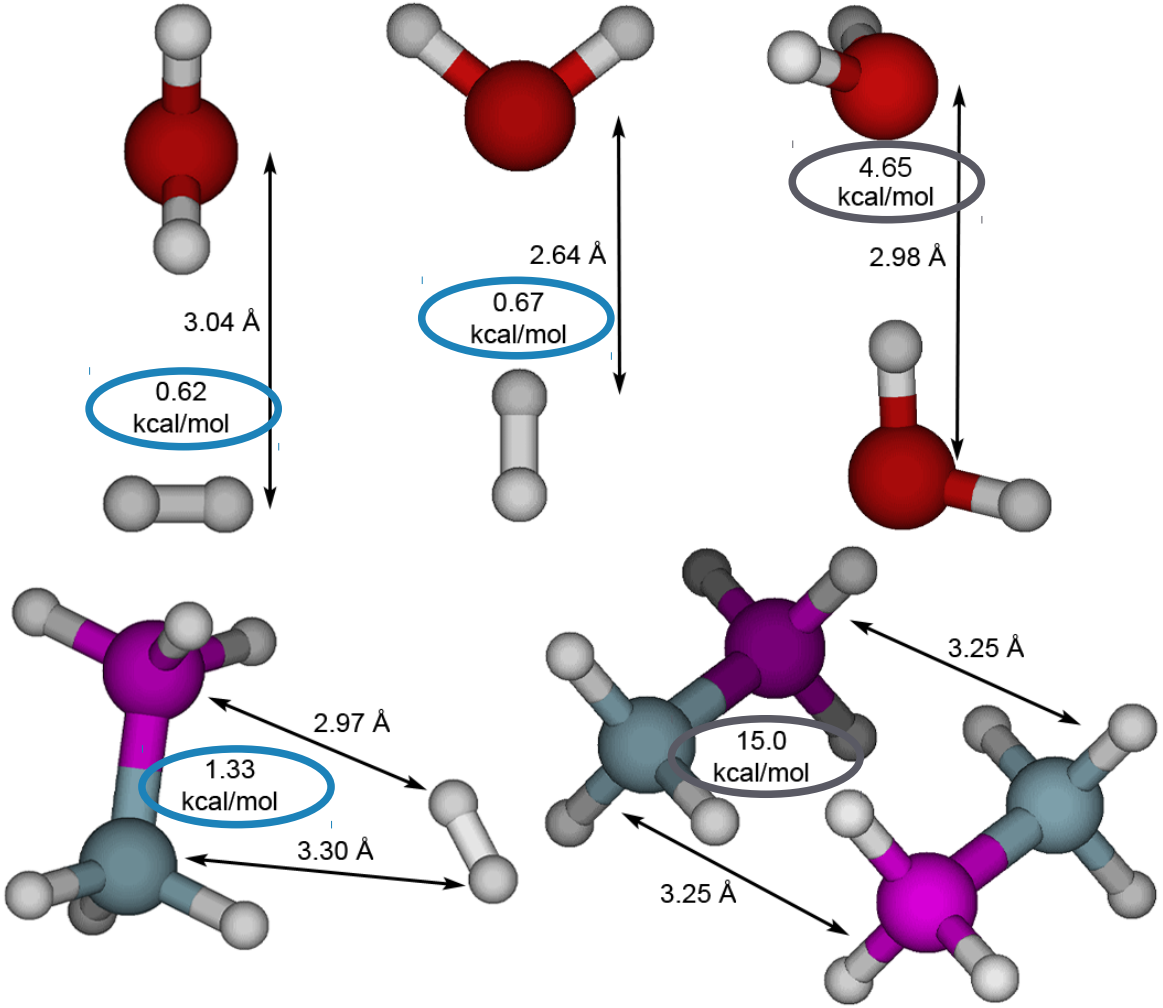
The concept of hierarchical hydrogen storage



CHSM – Chemical Hydrogen Storage Medium;
PA – Proton Acceptor;
PD – Proton Donor

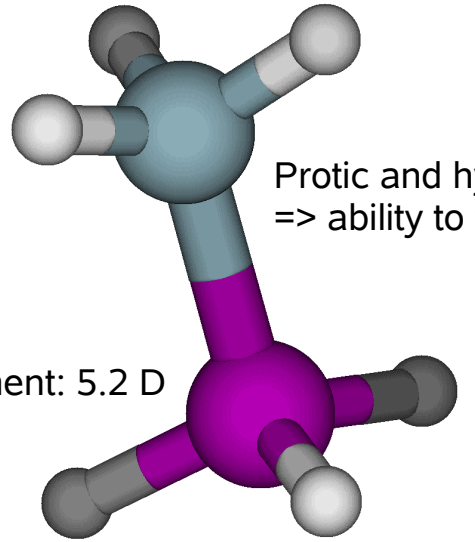
- Hydrogen clathrates built of Chemical Hydrogen Storage Medium (CHSM)
- CHSM (host) might be any chemical hydrogen storage material capable to form hydrogen bonded networks (complementary Proton Acceptor (PA) and Proton Donor (PD) sites)
- Kinetically easily accessible H_2 will fill in the clathrates further increasing the density of hydrogen
- Two steps of hydrogen release:
  - Fast: physisorbed H_2
  - Slow(er): decomposition of the CHSM framework

Ammonia borane as a host molecule



Design of AB clathrates. Formulation of the problem

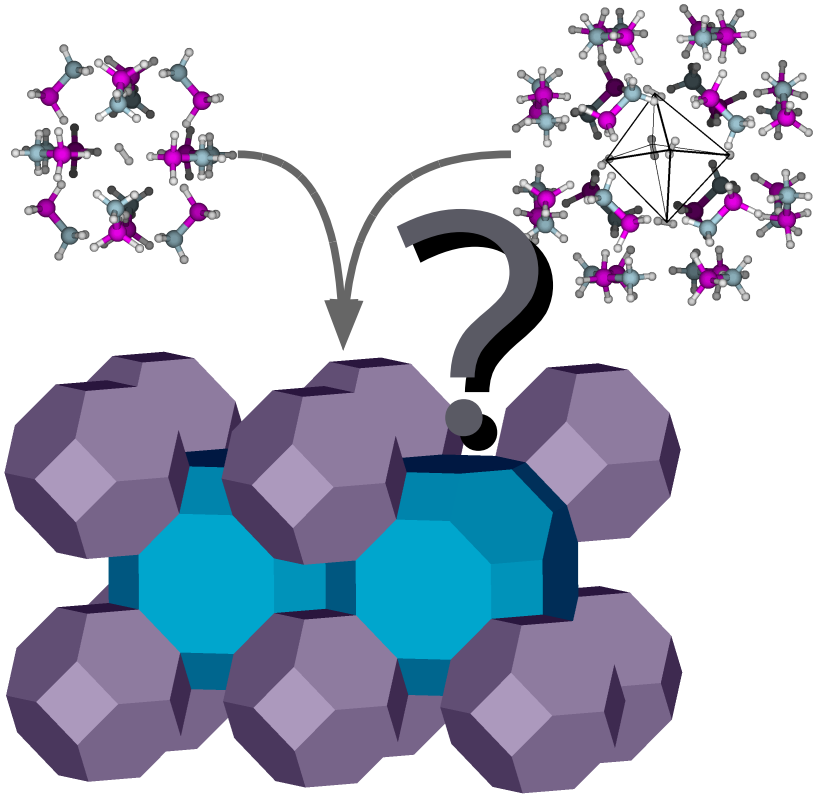
Given:



Protic and hydridic hydrogens
=> ability to form dihydrogen bonds

Dipole moment: 5.2 D

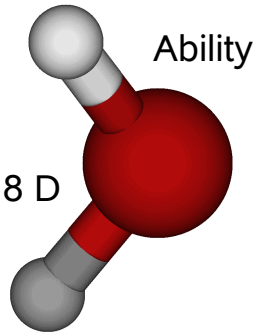
???:



- What are structures of clathrates of this material?
- What are conditions required to stabilize them?

An analogy and a reference

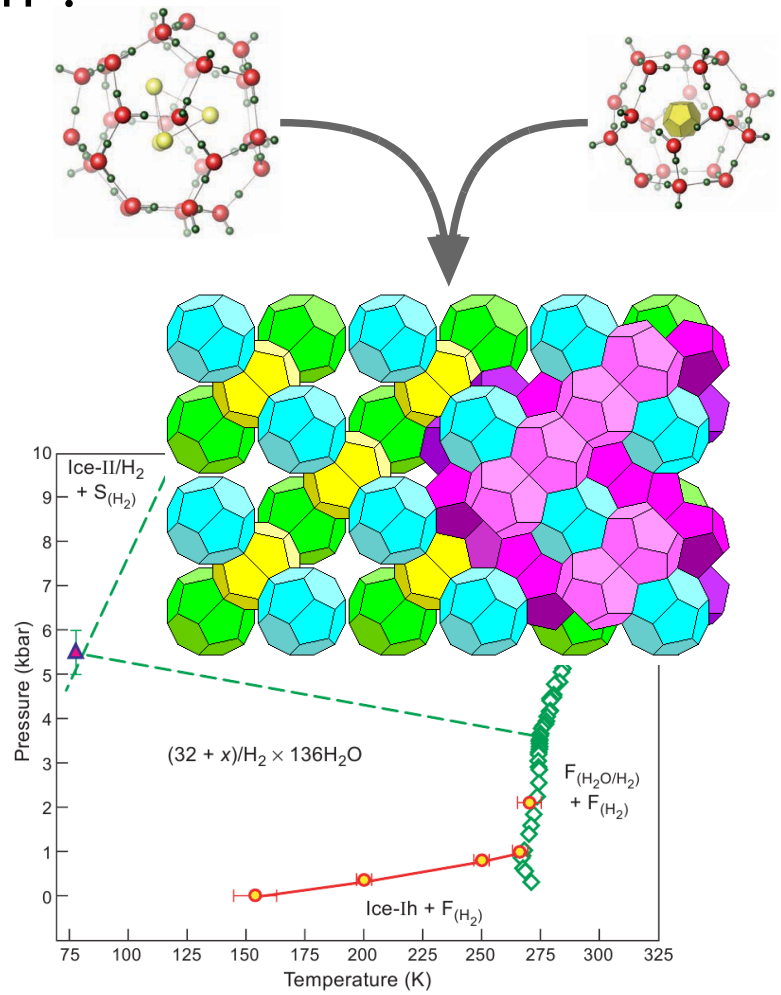
Given:



Ability to form hydrogen bonds

Dipole moment: 1.8 D

Known*:



* K. Lokshin and Y. Zhao, Los Alamos Science 30, 2006; Prof. Steve Dutch, University of Wisconsin-Green Bay

An analogy and a reference

- The Bernal-Fowler rules (or ice rules):

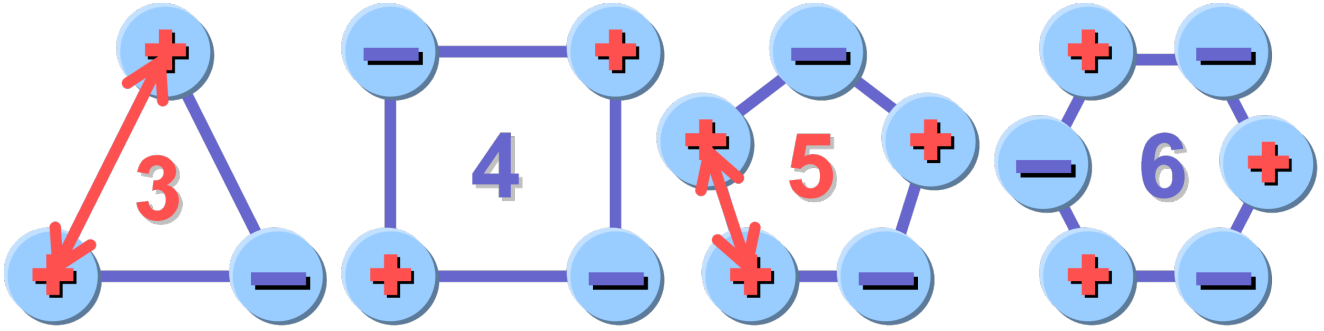
... ice consists of water molecules arranged so that each is surrounded by four others, each molecule being oriented in such a way as to direct its two hydrogen atoms toward two of the four neighbours, forming hydrogen bonds. The orientations are further restricted by the requirement that only one hydrogen atom lie near each O-O axis...

Linus Pauling, 1935

- X-ray studies of clathrate materials were pioneered by Herbert Powell in 1948. In earlier 50s crystal structures of hydrates have been resolved (Claussen 1951, Stackelberg and Muller 1951, Pauling and Marsh 1952)

What did we learn from hydrates, NH_3BH_3 molecule, and NH_3BH_3 crystal?

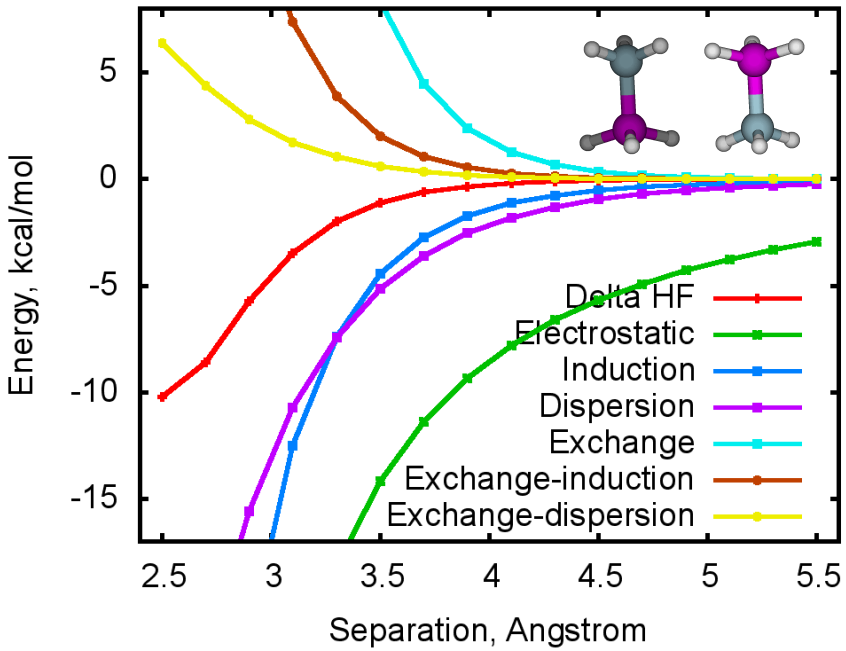
- Host molecules form convex polyhedrons
- NH_3 and BH_3 units of different molecules should be located somewhat opposite to each other
- Each hydrogen should be engaged into formation of two dihydrogen bonds
- Structural stability of polygons must be satisfied

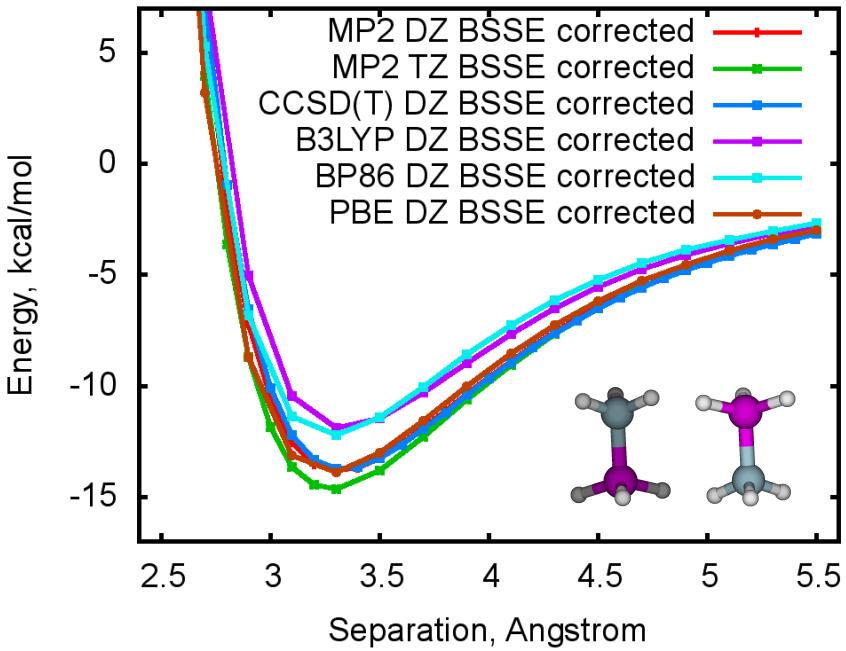


Used methods

- NH_3BH_3-H_2 interactions: SAPT, CCSD(T)
- NH_3BH_3 cages: DFT
- H_2 capacity of the cages: MP2, DFT-D
- Clathrate structures of NH_3BH_3: order-N DFT, plane wave methods, MD simulations

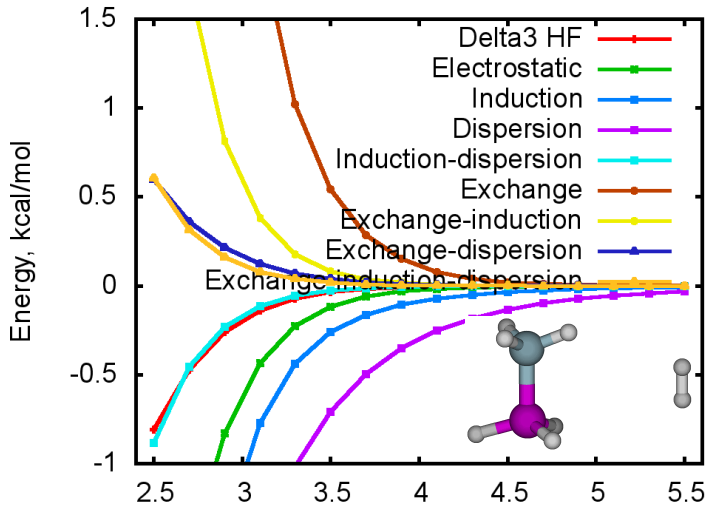
Host-host interactions

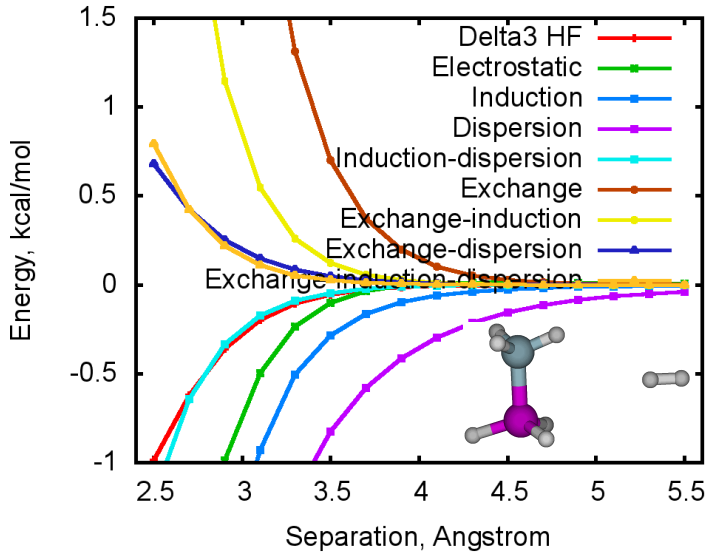


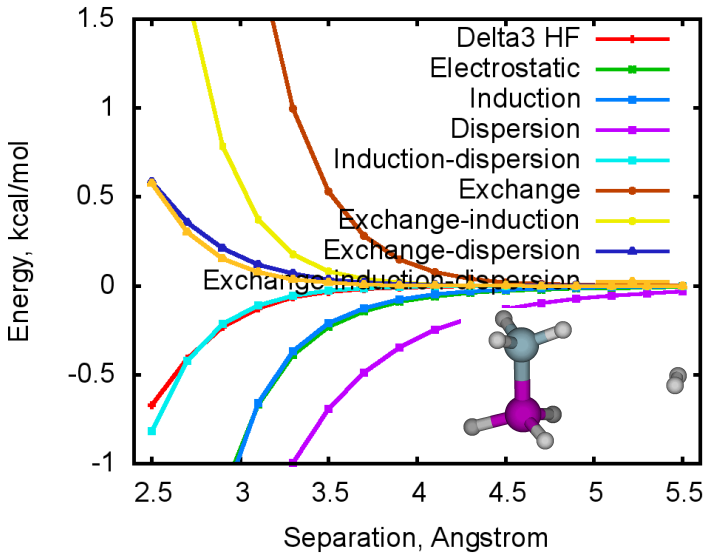


- The electrostatic part of interaction energy is dominant over other attractive components
- The DFT accuracy is comparable with MP2 and CCSD(T) methods with relative error within 15%
- PBE energy is practically identical to CCSD(T)
- The DFT can be used to design frameworks of ammonia borane clathrates

Host-guest interactions

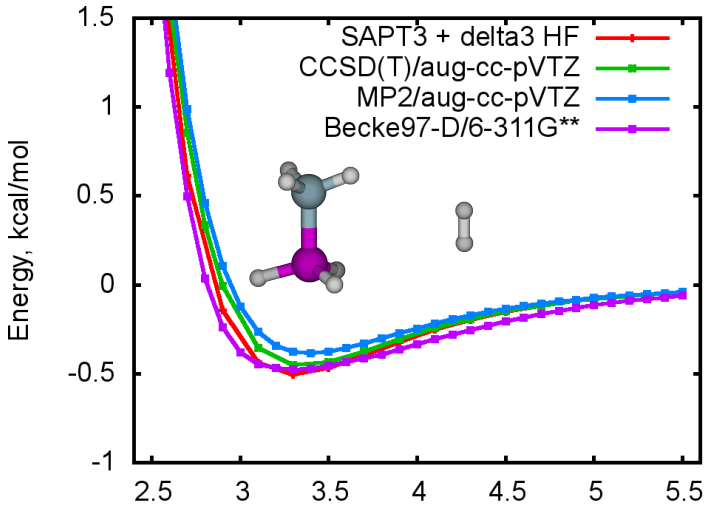


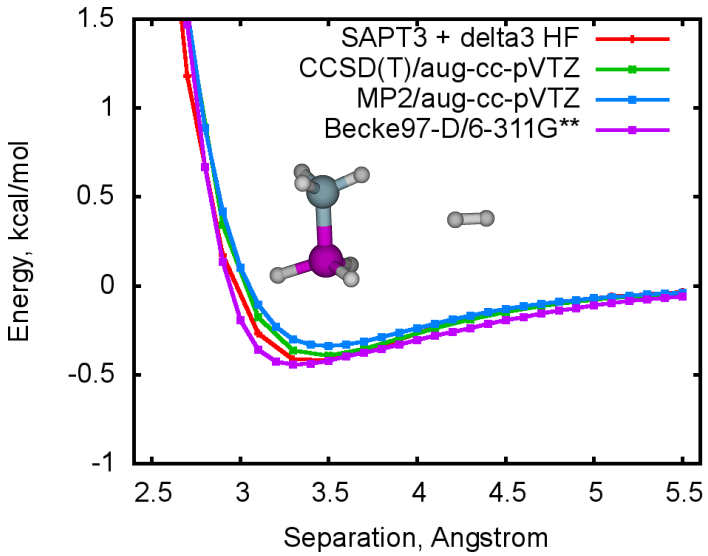


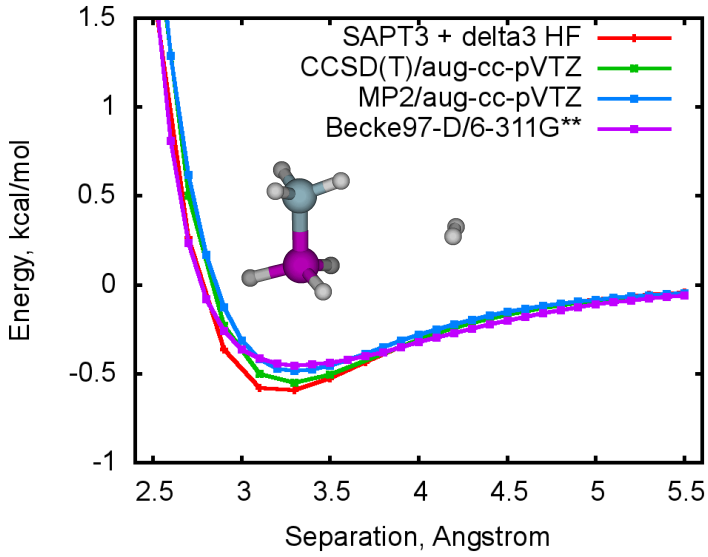


- For three configurations considered the dominant attractive part of interaction energy is dispersion

Host-guest interactions

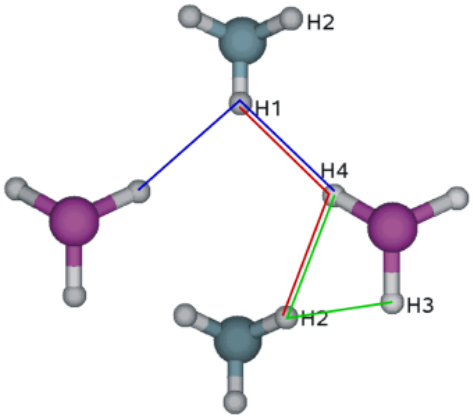




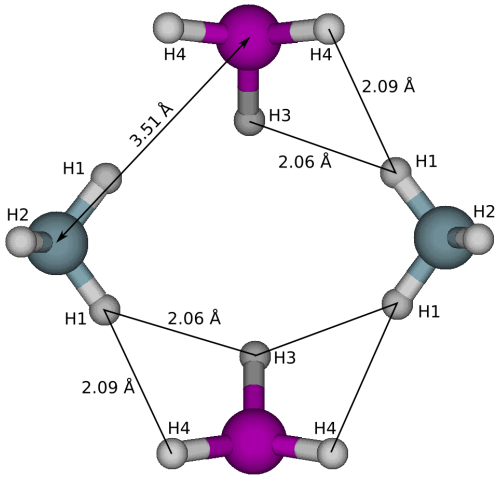


- The accuracy of the DFT-D and MP2 methods is in good agreement with the CCSD(T) and SAPT methods
- The DFT-D and MP2 methods can be used to estimate hydrogen capacity of ammonia borane clathrates

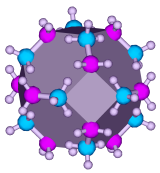
Possible cages of AB clathrates



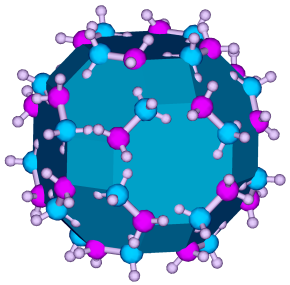
(b) Dihydrogen bonded network in orthorhombic AB, view along N-B bond with NH_3 units looking up and BH_3 units looking down (dihydrogen bonds of H1: blue; H2: green; H4: red).



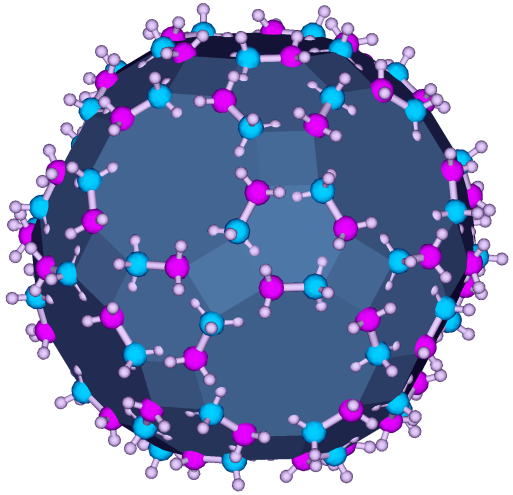
Dihydrogen bonded network in Cage 12



Truncated octahedron



Truncated cuboctahedron



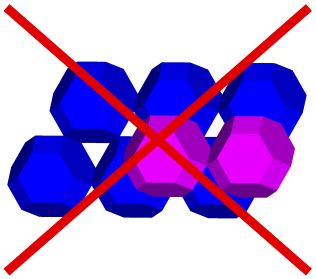
Truncated icosidodecahedron

Name	Cage 12	Cage 24	Cage 60
Specification	$4^6 6^8$	$4^{12} 6^8 8^6$	$4^{30} 6^{20} 10^{12}$
AB molecules per cage	12	24	60
Circumsphere diameter†, Å	10.80	14.39	22.28
BSSE corrected binding energy, kcal/mol	11.82	11.90	11.54

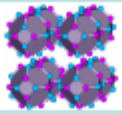
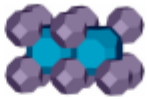
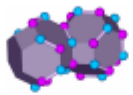
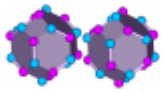
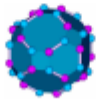
†The longest distance between two atoms in the cage

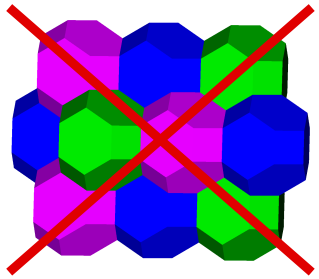
Level of theory: BP86(B3LYP)/6-311G**

Possible periodic structures of AB clathrates



Truncated alternated cubic

#	Name	Unit Cell[1]	Periodic Structure	Unit Cell Parameters[2]	Stability[3], kcal/mol
1	Cantitruncated Cubic Honeycomb			20.94x20.95x20.94 90.07x89.97x89.96 9186.55Å^3; 96 AB	0.318
2	Shared Hexagonal Faces			11.75x10.77x13.97 74.91x90.51x88.46 1706.22Å^3; 18 AB	1.491
3	Not Shared Tetragonal Faces I			11.63x11.63x20.83 90.69x89.99x90.00 2817.25Å^3; 24 AB	2.076
4	Not Shared Hexagonal Faces			11.80x10.87x10.58 74.37x90.36x89.47 1307.51Å^3; 12 AB	2.252
5	Omnitruncated Cubic Honeycomb			13.93x13.95x13.92 90.06x90.02x89.95 2704.22Å^3; 24 AB	2.253
6	Not Shared Octagonal and Tetragonal Faces			14.70x14.70x13.67 89.96x90.20x90.04 2953.73Å^3; 24 AB	2.398
7	Not Shared Tetragonal Faces II			22.43x22.42x22.43 89.89x89.81x90.01 11275.52Å^3; 60 AB	4.328

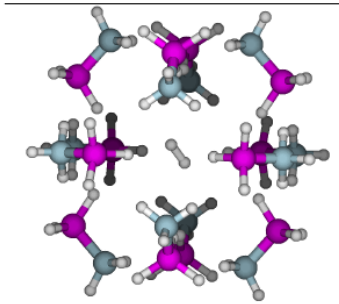
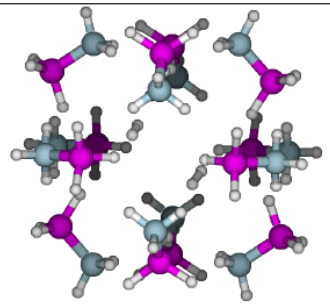
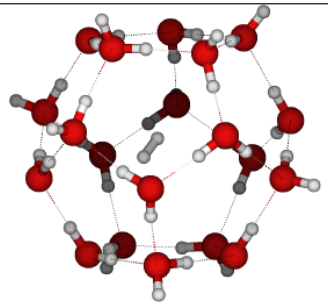
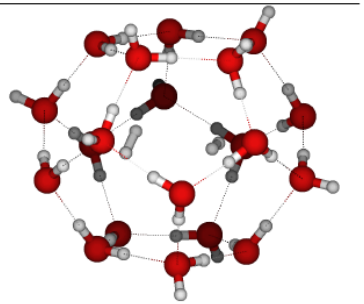


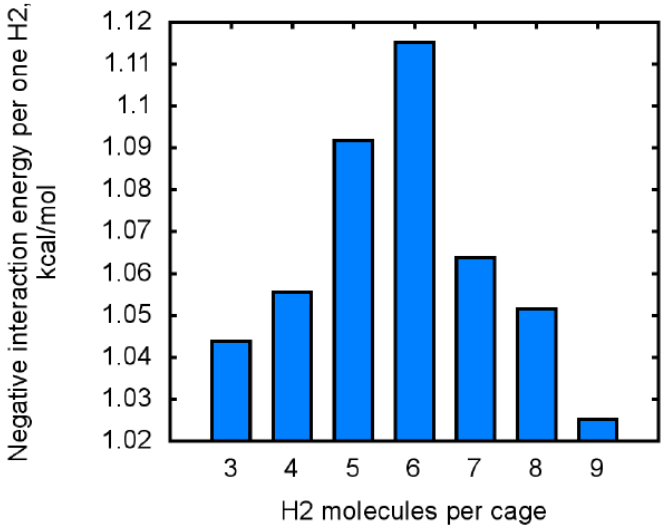
Bitruncated cubic

[1] Hydrogen atoms omitted for simplicity
[2] a x b x c, Å; alpha x beta x gamma, deg; volume; number of AB molecules
[3] Increase in ground state electronic energy per one AB molecule with respect to AB molecular crystal

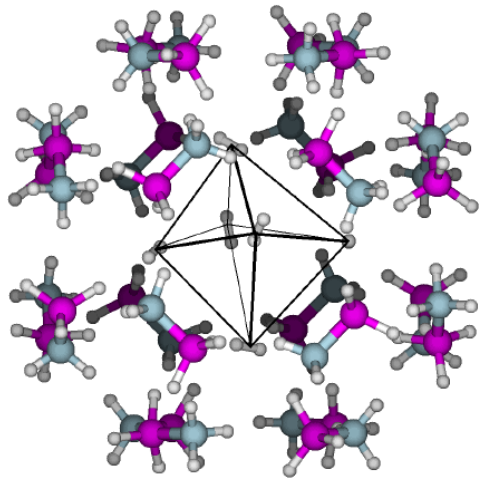
Level of theory: SIESTA PBE/DZP

Hydrogen capacity of AB clathrates

Cage 12		Small water cage	
$1H_2$@Cage	$2H_2$@Cage	$1H_2$@Cage	$2H_2$@Cage
			
-1.24 kcal/mol	4.01 kcal/mol	-1.31 kcal/mol	1.13 kcal/mol



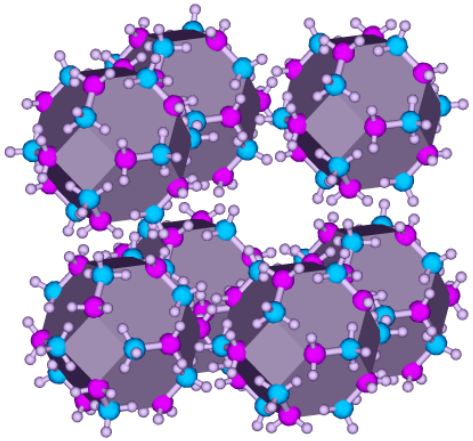
(a) Specific interaction energy of molecular hydrogen enclosed in Cage 24.



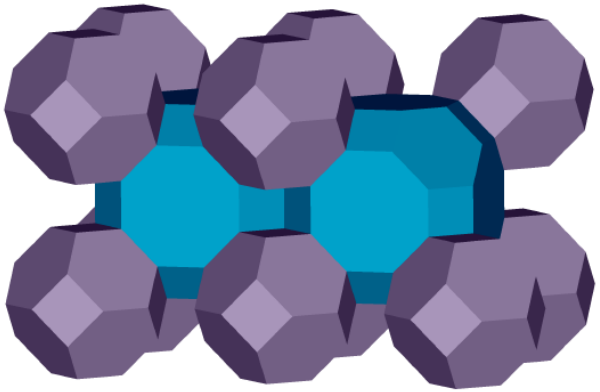
(b) Octahedral orientation of H_2 molecules enclosed in Cage 24.

Level of theory: MP2/aug-cc-pVDZ, Becke97-D/6-311G**

Hydrogen capacity of AB clathrates



(a) Connection of cages in unit cell of the CCH structure of AB clathrates (one Cage 12 and faces of Cages 24 are removed).



(b) Periodic structure of the CCH framework of AB clathrates (all cages are shown explicitly).

Material	Unit cell volume, Å^3	Unit cell formula	Density†, g/cm^3	Weakly bound H_2, wt%	Strongly bound H_2, wt%	Total H_2, wt%
CCH structure of AB clathrates	9186.6	$32H_296NH_3BH_3$	0.55/0.12	2.1	19.2	21.3
Molecular crystal of AB	131.5	$2NH_3BH_3$	0.78/0.15	0	19.6	19.6

†Volumetric density of the material itself / of the hydrogen

The CCH structure and AB molecular crystal

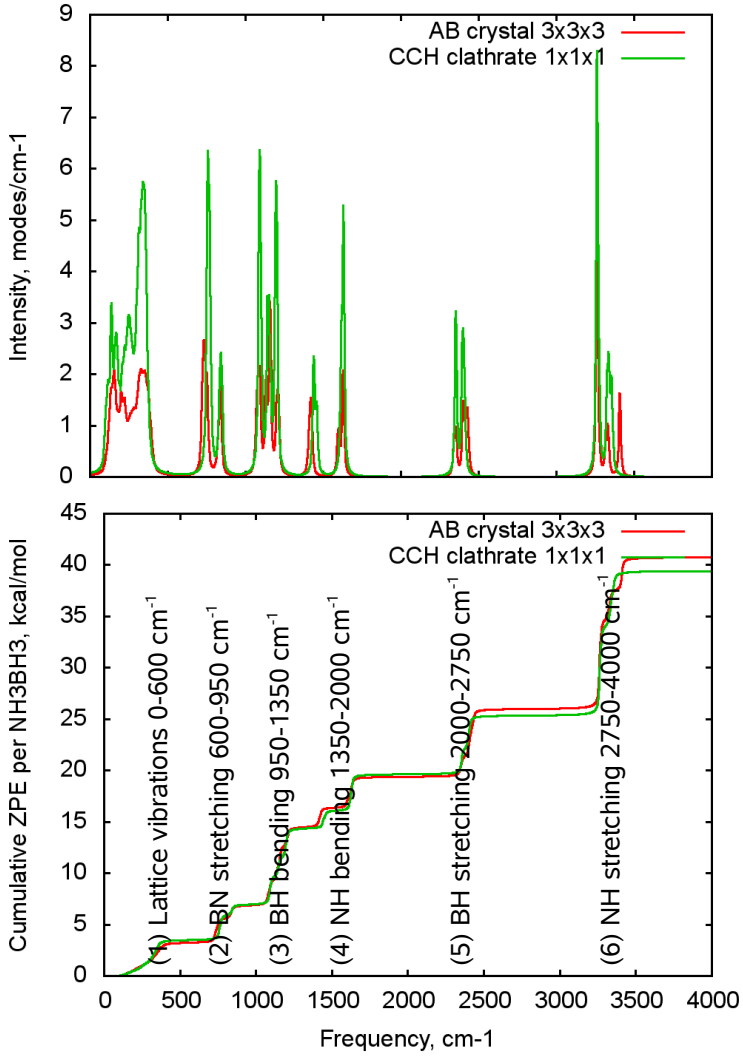
Electronic energy of the CCH structure computed with VASP/PBE is 0.5 kcal/mol lower (per formula unit) than corresponding value computed for AB molecular crystal!!!

Finite temperature effects:

- *Ab initio* MD for 7.5 ps
- Construction of the velocity autocorrelation function
- Fourier transform of the VAF to get phonon DOS

- 3K: CCH is more stable by 1.8 kcal/mol
- 77K: CCH is less stable by 0.5 kcal/mol

Phonon density of states (at 3K) and cumulative ZPE



Van der Waals and Platteeuw (1959) model and hydrogen hydrates

- The grand canonical partition function for water used in the model is derived based on assumptions which are incompatible with hydrogen hydrates
  - Each cavity can contain at most one guest molecule
  - No quantum effects are needed and classical statistics are valid
- The model significantly underestimates dissociation pressure of hydrogen hydrates

Guest molecule	Hydrate structure	Published data† T, °C; P, atm	Calculated P, atm
Xe	I	0; 1.5	1.5
CO_2	I	0; 12.4	12.4
CH_4	I	-0.2; 25.3	28.6
C_2H_6	I	-0.03; 5.23	4.2
C_3H_8	II	0; 1.74	1.6
N_2	II	-1.3; 141.5	128.4
H_2	II	-3.15; 2072.5§	1087.1

Main equations:

$$\Delta\mu_W^\alpha = \mu_W^\beta - \mu_W^H = \mu_W^\beta - \mu_W^\alpha$$

$$\mu_W^H = -kT\left(\frac{\partial ln\Xi}{\partial N_W}\right)_{T,V,\lambda_J} = \mu_W^\beta + kT\sum_i \upsilon_i ln\left(1-\sum_J \theta_{J,i}\right)$$

$$\theta_{J,i} = \frac{C_{J,i}P_J}{1+\sum_J C_{J,i}P_J} \qquad C_{J,i} = \frac{4\pi}{kT}\int_0^{R_c}\exp\left(-\frac{w(r)}{kT}\right)r^2dr$$

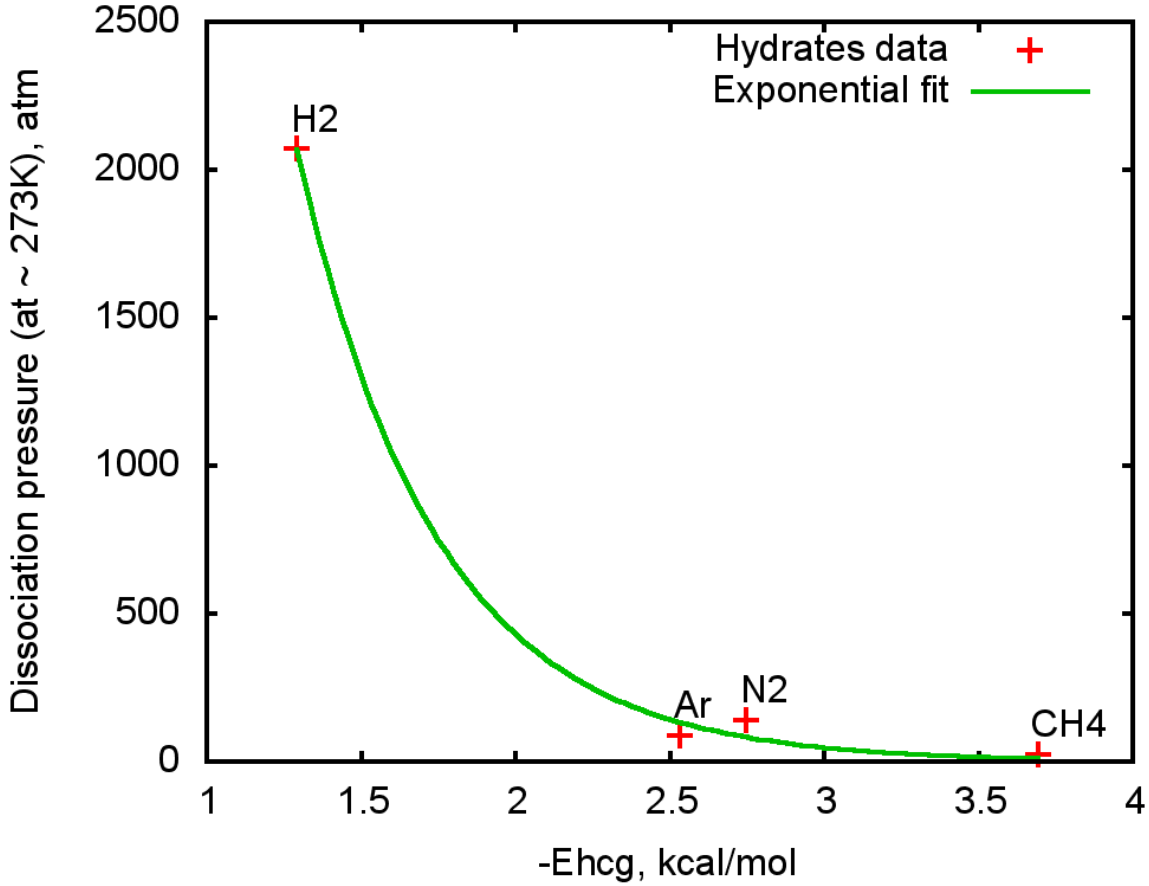
$$\frac{\Delta\mu_W^\alpha(T,P_R)}{RT} = \frac{\Delta\mu_W^\alpha(T_0,P_0)}{RT_0} - \int_{T_0}^{T}\frac{\Delta h_W^\alpha}{RT^2}dT + \int_{T_0}^{T}\frac{\Delta v_W^\alpha}{RT}\frac{dP}{dT}dT$$

$$= \frac{\Delta\mu_W^\alpha(T_0,P_0)}{RT_0} - \int_{T_0}^{T}\frac{\Delta h_W^\alpha}{RT^2}dT + \int_{P_0}^{P_R}\frac{\Delta v_W^\alpha}{RT}dP$$

$$\Delta\mu_W^\alpha(T,P) = \Delta\mu_W^\alpha(T,P_R) + \Delta v_W^\alpha(P-P_R)$$

Linking PT stability of clathrates and weak intermolecular interactions

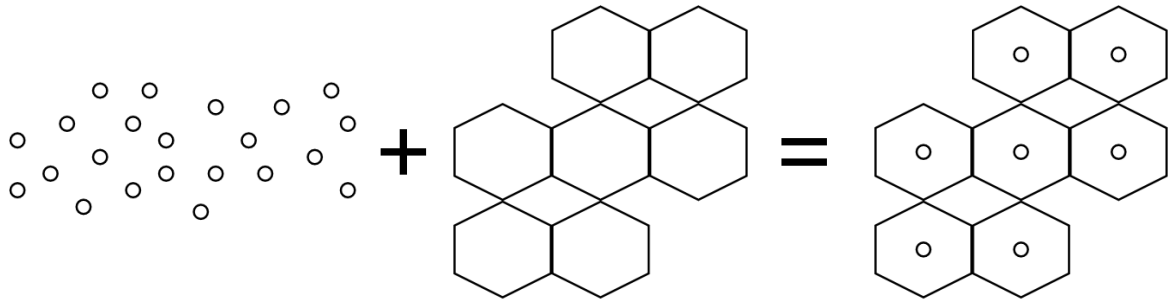
Correlation between host cage-guest molecule interaction energy and stability of hydrates



Linking PT stability of clathrates and weak intermolecular interactions

Free energy change for process of enclathration:

$$\mathrm{Gas} + \mathrm{Cage} \rightarrow \mathrm{Gas@Cage}$$



$$\triangle G = \triangle H - T\triangle S \approx$$

$$\approx E_{HCG} - T(S_{PSB} - S_{ST}) = 0$$

Main assumptions:

(i) Empty clathrate is as stable as molecular crystal;

(ii) Gas phase particles do not interact;

(iii) Small cages are the weakest elements of the clathrate structure.

E_{HCG} – the interaction energy between host cage and guest molecule;

S_{PSB} – the entropy of a particle in a spherically symmetric rectangular potential well (the entropy of a particle in a spherical box);

S_{ST} – the Sackur-Tetrode entropy of ideal gas.

Linking PT stability of clathrates and weak intermolecular interactions

- The interaction energy between the host cage and the guest molecule

$$E_{HCG} = E_{complex} - E_{cage} - E_{guest} + \triangle E_{cage} + \triangle E_{guest}$$

$$\triangle E_m = E_m(\text{complex geometry}) - E_m(\text{monomer equilibrium geometry})$$

- The Sackur-Tetrode entropy of ideal gas

$$S_{ST} = R\ ln\left(\frac{e^{5/2}V}{N_A \Lambda^3}\right)$$

with volume calculated from the van der Waals equation of state

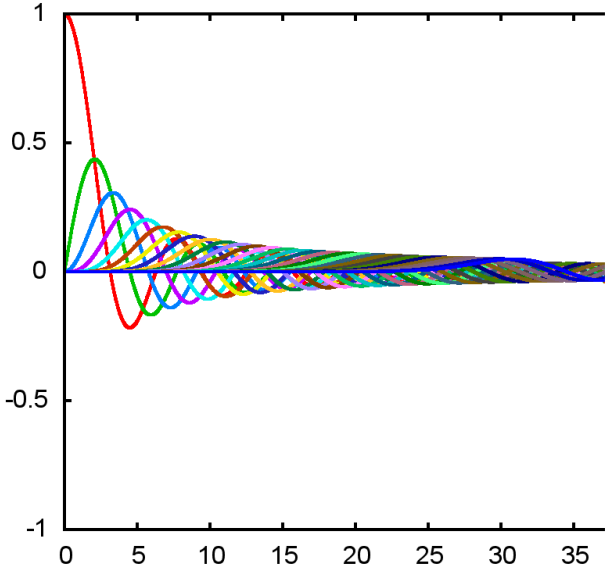
$$V = \frac{RT}{P + a/V^2} + b$$

Linking PT stability of clathrates and weak intermolecular interactions

- The entropy of a particle in a spherical box

$$S_{PSB} = \frac{U - U(0)}{T} + k\ lnQ \qquad U = U(0) - \left(\frac{\partial lnQ}{\partial \beta}\right)_V$$

$$Q = q^N \qquad q = \sum_i g_i \exp\left(-\frac{E_i}{kT}\right) \qquad E_{nl} = \frac{\hbar^2 X_{nl}^2}{2\mu r_s^2}$$

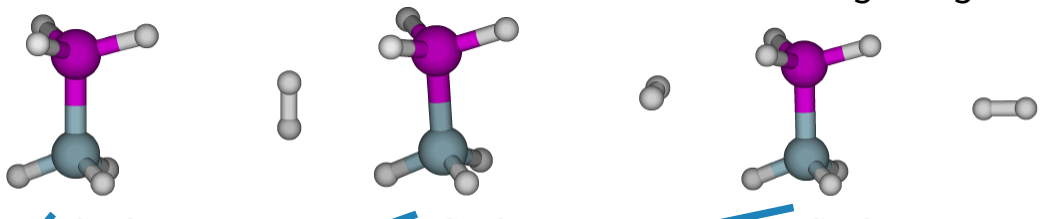


X_{nl} are the roots of the spherical Bessel function;
n is the number of the root of the function, the principle quantum number;
l is the order of the function, the angular momentum quantum number.

$$j_l(z) = 2^l z^l \sum_{p=0}^{\infty} \frac{(-1)^p (p+l)!}{p!(2p+2l+1)!} z^{2p} = z^l \left(-\frac{1}{z}\frac{d}{dz}\right)^l \frac{\sin z}{z}$$

Linking PT stability of clathrates and weak intermolecular interactions

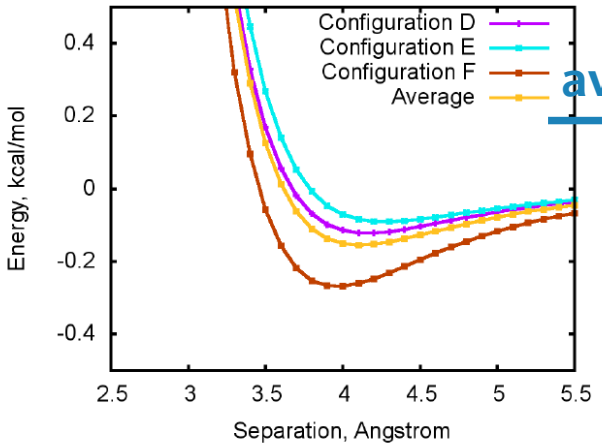
- Radius of the spherical box – clathrates of NH_3BH_3



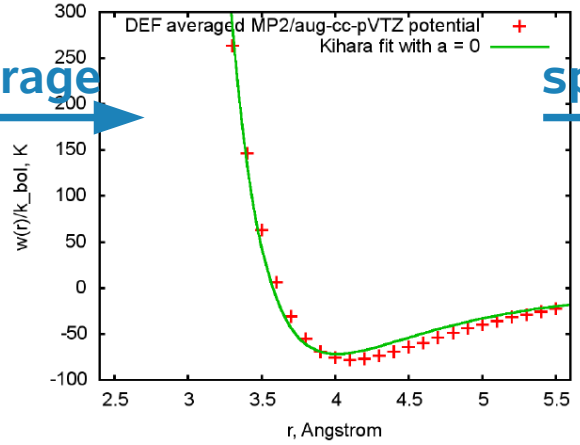
$$\Phi(r) = 4\epsilon\left[\left(\frac{\sigma}{r-2a}\right)^{12} - \left(\frac{\sigma}{r-2a}\right)^{6}\right]$$

$$w(r) = 2Z\epsilon\left[\frac{\sigma^{12}}{R_c^{11}r}\left(\delta^{10} + \frac{a}{R_c}\delta^{11}\right) - \frac{\sigma^{6}}{R_c^{5}r}\left(\delta^{4} + \frac{a}{R_c}\delta^{5}\right)\right],$$

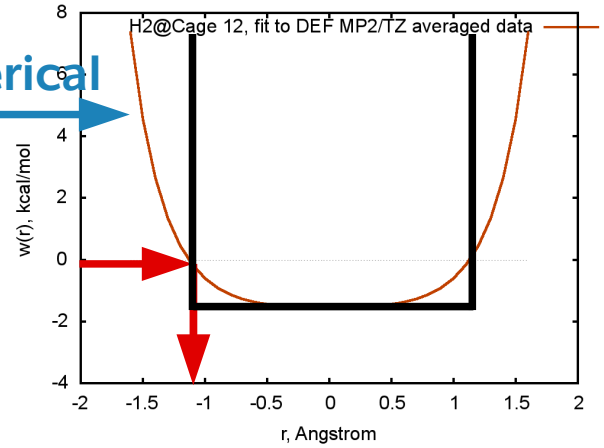
$$\text{where } \delta^M = \frac{1}{M}\left[\left(1 - \frac{r}{R_c} - \frac{a}{R_c}\right)^{-M} - \left(1 + \frac{r}{R_c} - \frac{a}{R_c}\right)^{-M}\right]$$



average



spherical



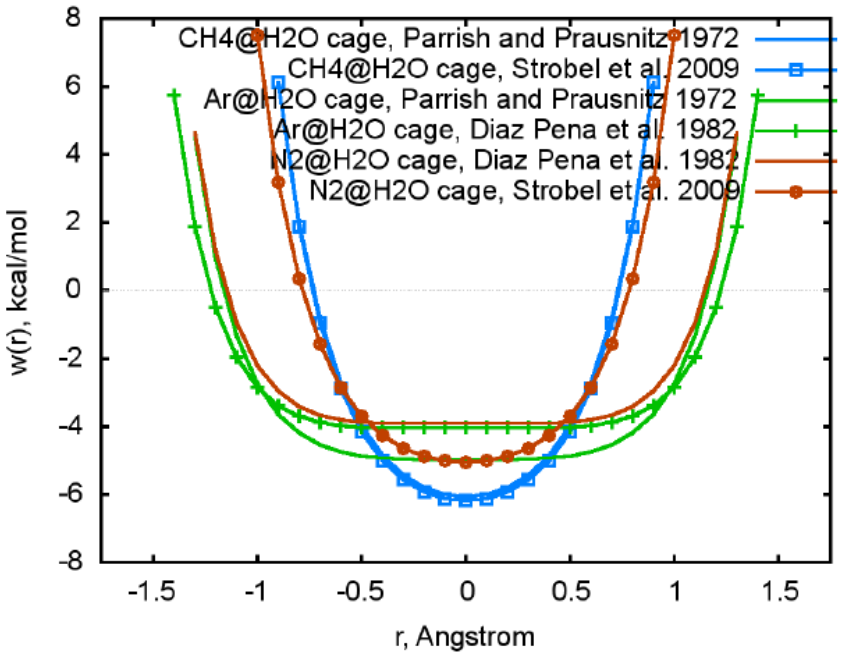
AB-H2 intermolecular potentials

Kihara fit to AB-H2 average potential

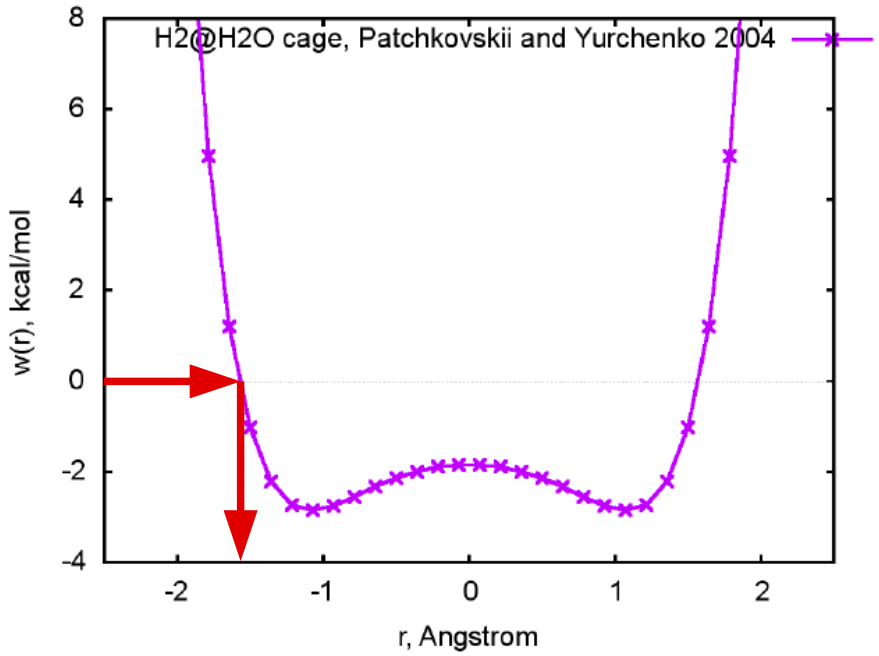
Effective radius of the cage potential

Linking PT stability of clathrates and weak intermolecular interactions

- Radius of the spherical box – hydrates of CH_4, Ar, N_2, and H_2



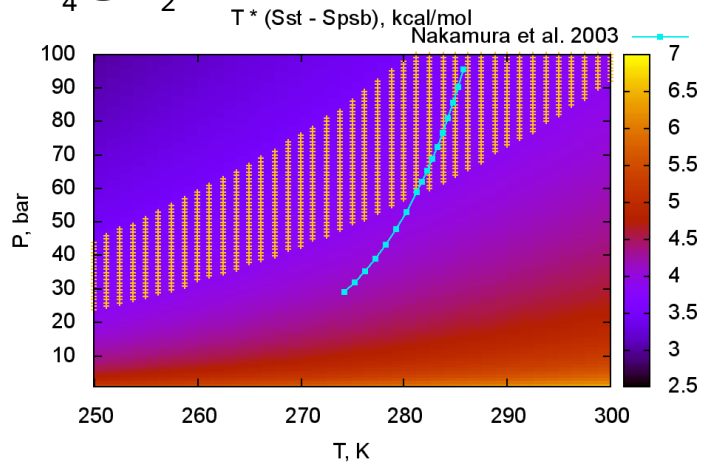
(a) Small cavity empirical potentials of CH_4, Ar, and N_2 hydrates



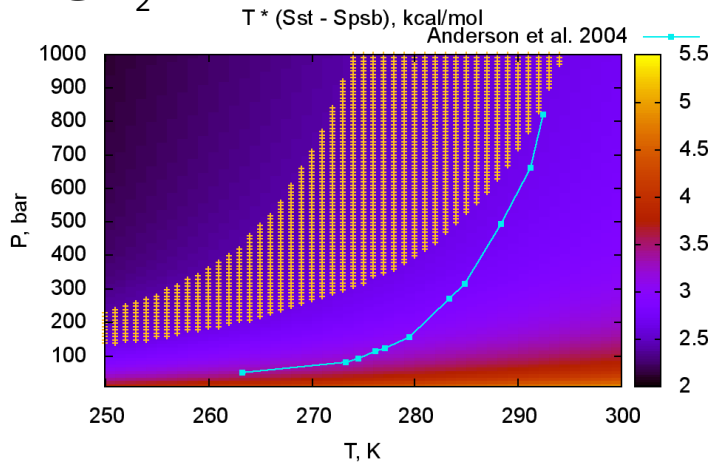
(b) Small cavity ab-initio potential of H_2 hydrates

Applications of the statistical model

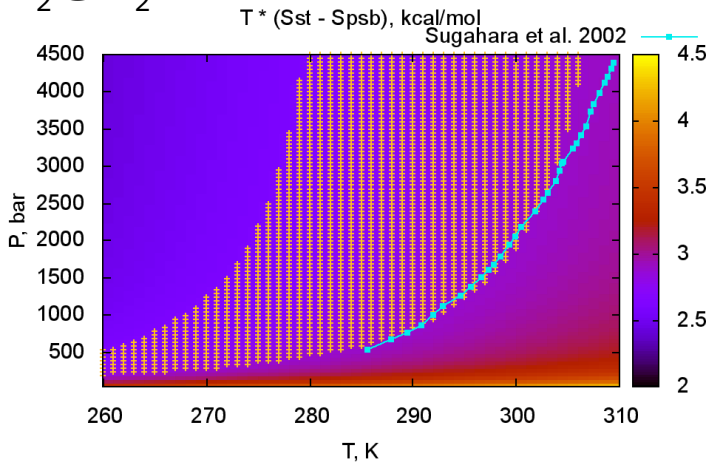
$CH_4@H_2O$



$Ar@H_2O$



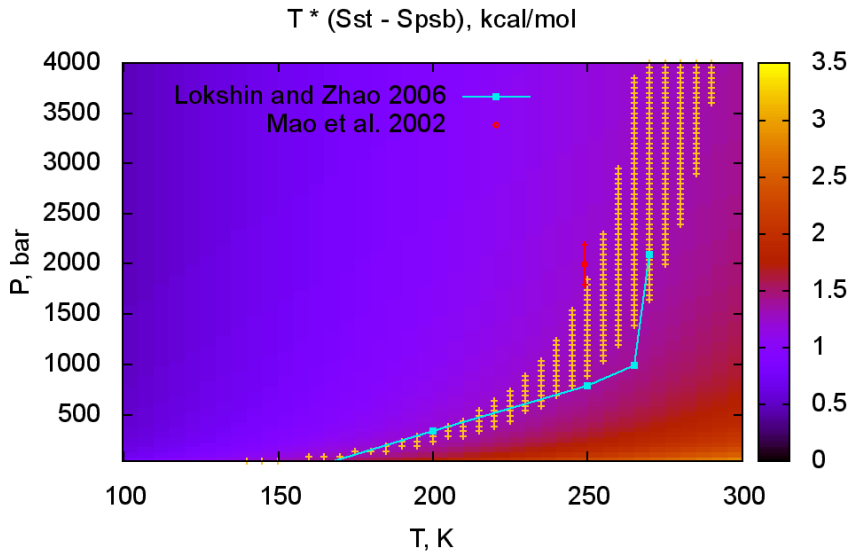
$N_2@H_2O$



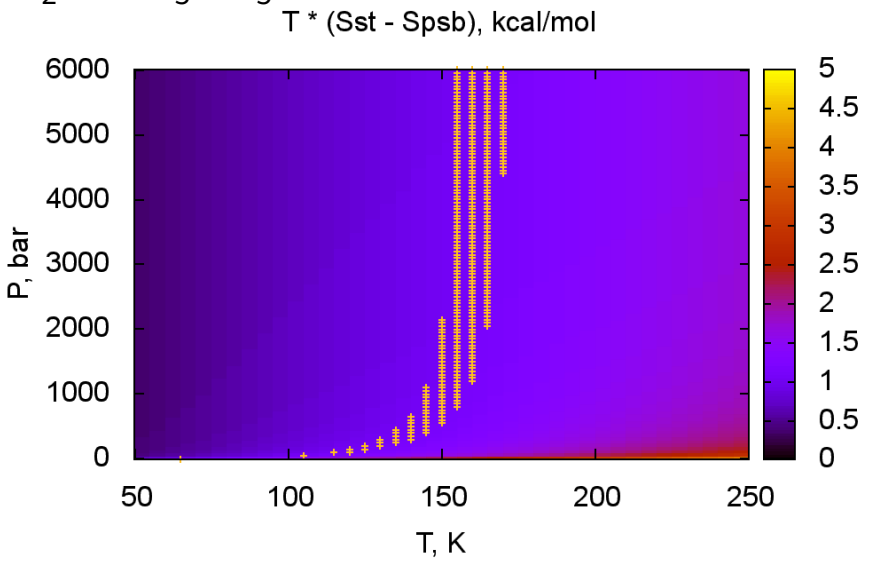
- The term $-T(S_{PSB}-S_{ST})$ is shown in a form of colour map depending upon P and T
- The term $-E_{HCG}$ +/− 5% is shown as a highlighted region
- Real hydrate stability zone extends from light blue line towards left and top

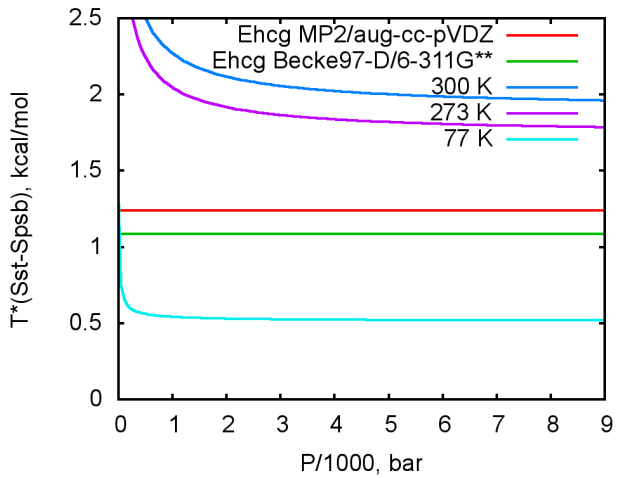
Applications of the statistical model

$H_2@H_2O$



$H_2@NH_3BH_3$





- The model predicts stability of hydrogen hydrates in good agreement with experiment
- NH_3BH_3 clathrates could be stabilized at 77K at ambient pressure

Summary of results on clathrates of AB

- Structures of clathrates of ammonia borane have been envisaged and their relative stabilities have been calculated
- A statistical model of clathrate phase equilibria has been developed that is based on calculated guest-host interactions, entropy of guest molecules in spherical cages, and corrections for nonideality of gases
- Applicability of the model have been tested on known hydrates of CH_4, Ar, N_2, and H_2. Quantitative agreement between experimental data and theoretical predictions could be expected for small guest molecules below ice melting point
- Pressures required for room temperature hydrogen storage in small cages of clathrate structures are practically unattainable. Clathrates of ammonia borane loaded with hydrogen could be stabilized at ambient pressure by lowering temperature down to 77 K

1. A. Abramov and M. Gutowski, Stability of hydrogen clathrates of ammonia borane, Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem. 55 (1), (2010).
2. A. Abramov and M. Gutowski, Structure and stability of hydrogen clathrates of ammonia borane, Mater. Res. Soc. Symp. Proc., Boston, MA, November 30 - December 4, 2009.
3. M. Gutowski and A. Abramov, Hierarchical storage of hydrogen in clathrates of ammonia borane, Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem. 2009, 54 (2).

Experimental work on AB clathrates

- Lin et al., PNAS, 2009
  - A solid phase, $NH_3BH_3(H_2)_x$, x = 1.3-2, has been discovered at excess hydrogen pressure of 6.2 GPa
- Chellappa et al., J. Chem. Phys. 131, 2009
  - Excited H_2 stretching modes are ascribed to the H_2 molecules stabilized at 6.7 and 10 GPa in the NH_3BH_3 lattice voids

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