Transport and selectivity properties in clathrate hydrates

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HyDfect et MI²C

Groupe Spectroscopie Moléculaire et Plateforme SIV

Spectroscopies de Vibration

IR (9)

- 1 IRTF (MIR) + ATR, DRIFT …
- 2 IRTF (MIR) + PM-IRRAS
- 1 IRTF (MIR) + VCD
- 1 IRTF (MIR-LIR) + montage cryogénique
- 1 IRTF (MIR-PIR) + montage HP (milieux supercritiques)
- 1 IRTF (MIR) portable
- 1 IRTF (MIR-LIR) + microscope IR
- 1 IRTF (MIR) + imageur IR

Raman (10)

- 6 µ-Spectromètres [325-1064] nm
- 1 Raman/AFM, TERS
- 1 ROA
- 1 µ-SHG/µ-Raman
- 1 Raman/hyper-Raman et hyper-Rayleigh (montage 90°)
- Platines µ-thermiques BT et HT
- Platine de µ-polarisation
- Platine µ-pression HP-BT

Photonique et Fonctionnalité

Applications et développements expérimentaux

Physico-chimie pour le Développement durable

Stockage et production d'énergie

Spectroscopies UV-Visible

- Fluorescence (Spex, Fluorolog 3)
- Absorption (Perkin Elmer, Phillips, Shimadzu, Ocean Optics) :Montage µ-absorption [400-900] nm

Mesures optiques linéaires et non linéaires

- Constantes optiques dans le visible et l'IR de matériaux massiques et multicouches (Réflexion, ATR, M-Lines)
- 2 montages SHG en transmission et réflexion à 1064 nm et 1550 nm
- Hyperpolarisabilités (1064 nm)

Microscopie à Force Atomique (AFM)

- Autoprobe CP-Research
- Agilent 5500 AFM
- Bruker Dimension Icon
- SNOM

Grands instruments

- Diffusion neutrons et Absorption X

Cellule de transfert: SAFIRR
Liens industriels

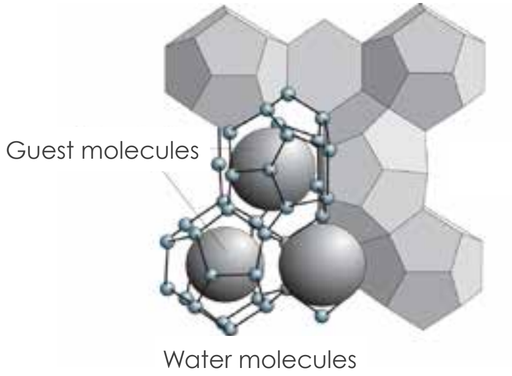
http://gsm.ism.u-bordeaux1.fr

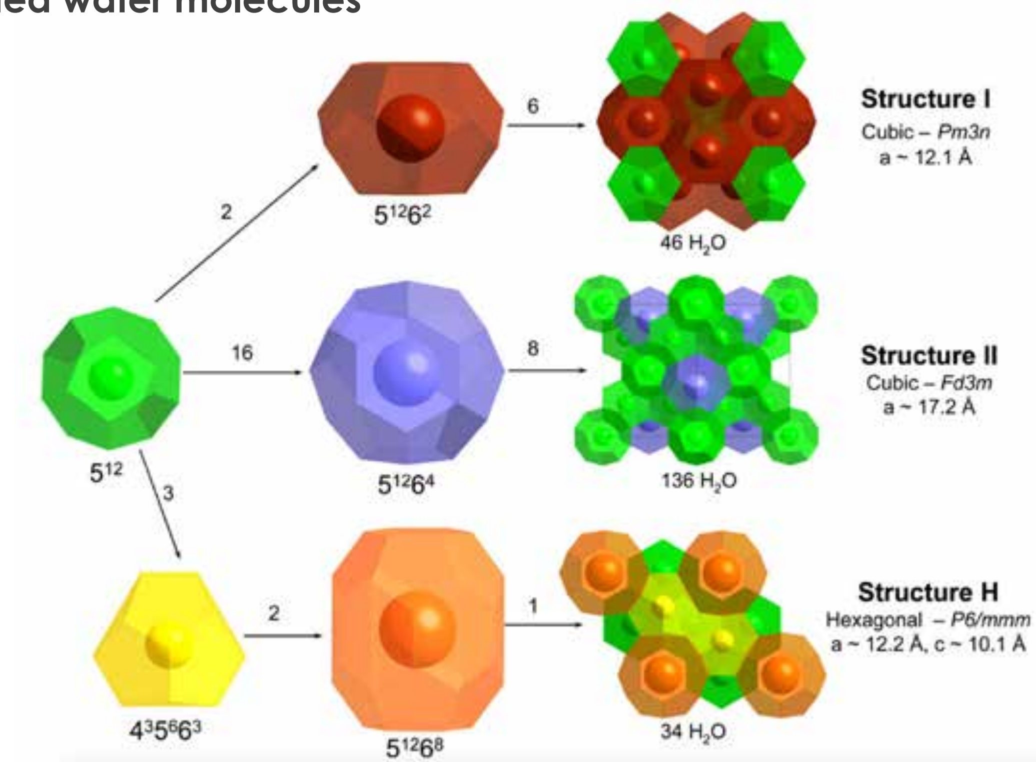
Contents

- ***Clathrate hydrates***
- ***Methodology***
- ***Hydrogen diffusion in the THF-H_2 clathrate hydrate***
- ***Selectivity in the CO-N_2 clathrate hydrate***
- ***Concluding remarks***

Structural properties of clathrate hydrates.

✓ **Building host cages from H-bonded water molecules**





⇨*Various clathrates structures depending on formation conditions, guest nature, etc….*

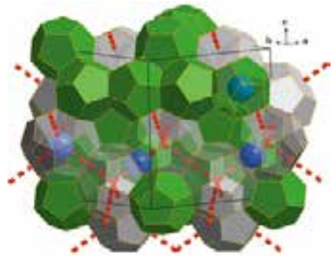
E.D. Sloan, C. Koh, *Clathrate Hydrates of Natural Gases* (2008)

T.A. Strobel et al., Chem. Phys. Letters **478** (2009) 97–109

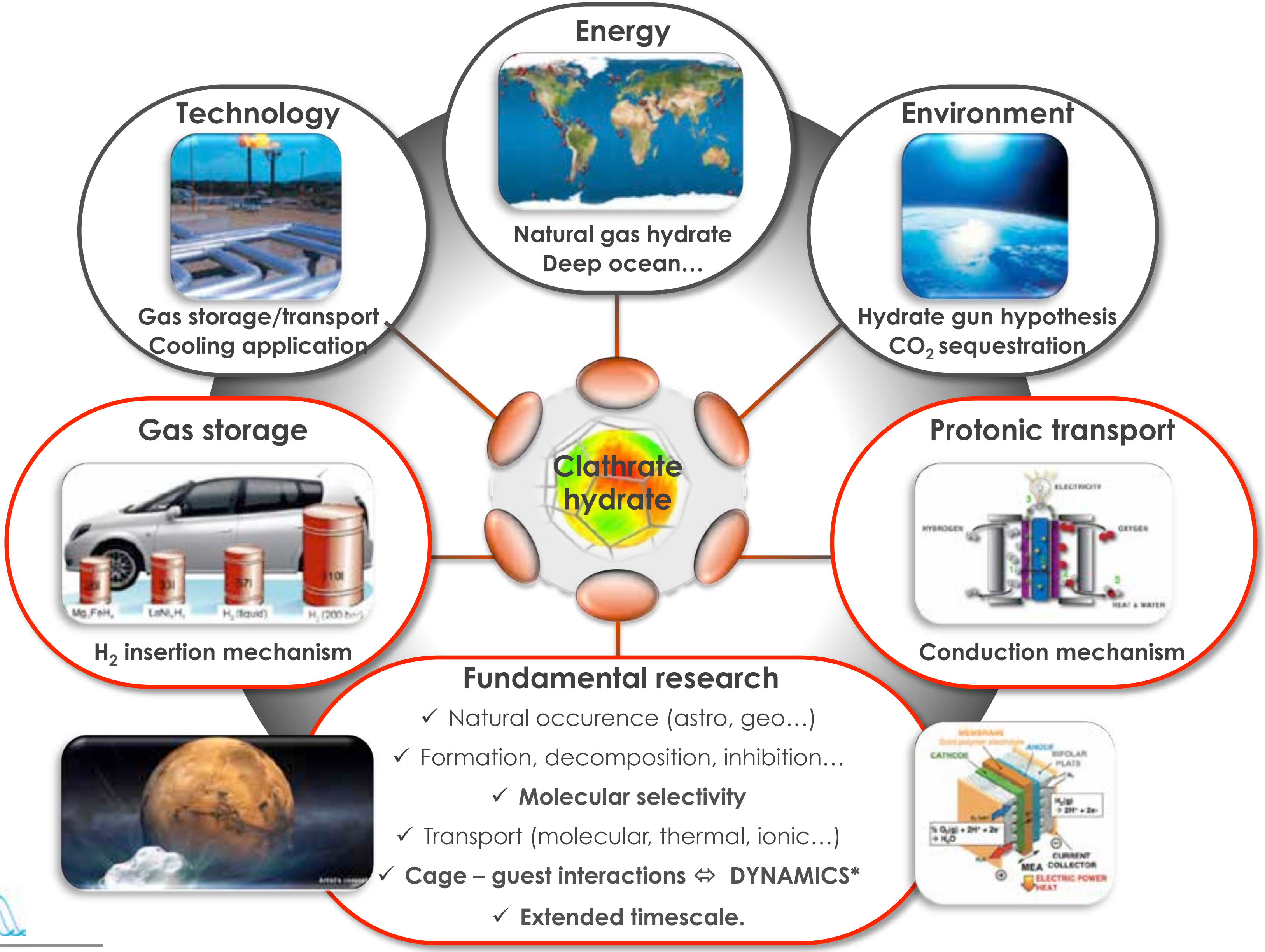
✓ ***Stable only with guests until last year…***

…Ice phase XVI: clathrate with empty cages

Neutron Diffraction onto vacuum-pumped neon clathrate hydrate.
A. Falenty, *et al*, Nature **516** (2014) 231–233.

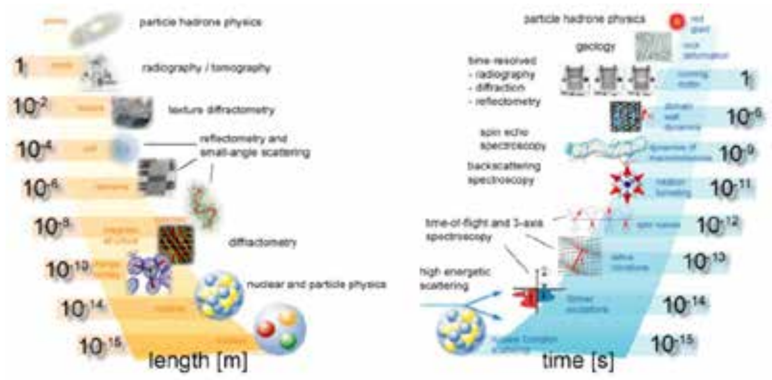


Scientific case



*e.g. A. Desmedt *et al*, *Eur. Phys. J. Special Topics* **213** (2012) 103

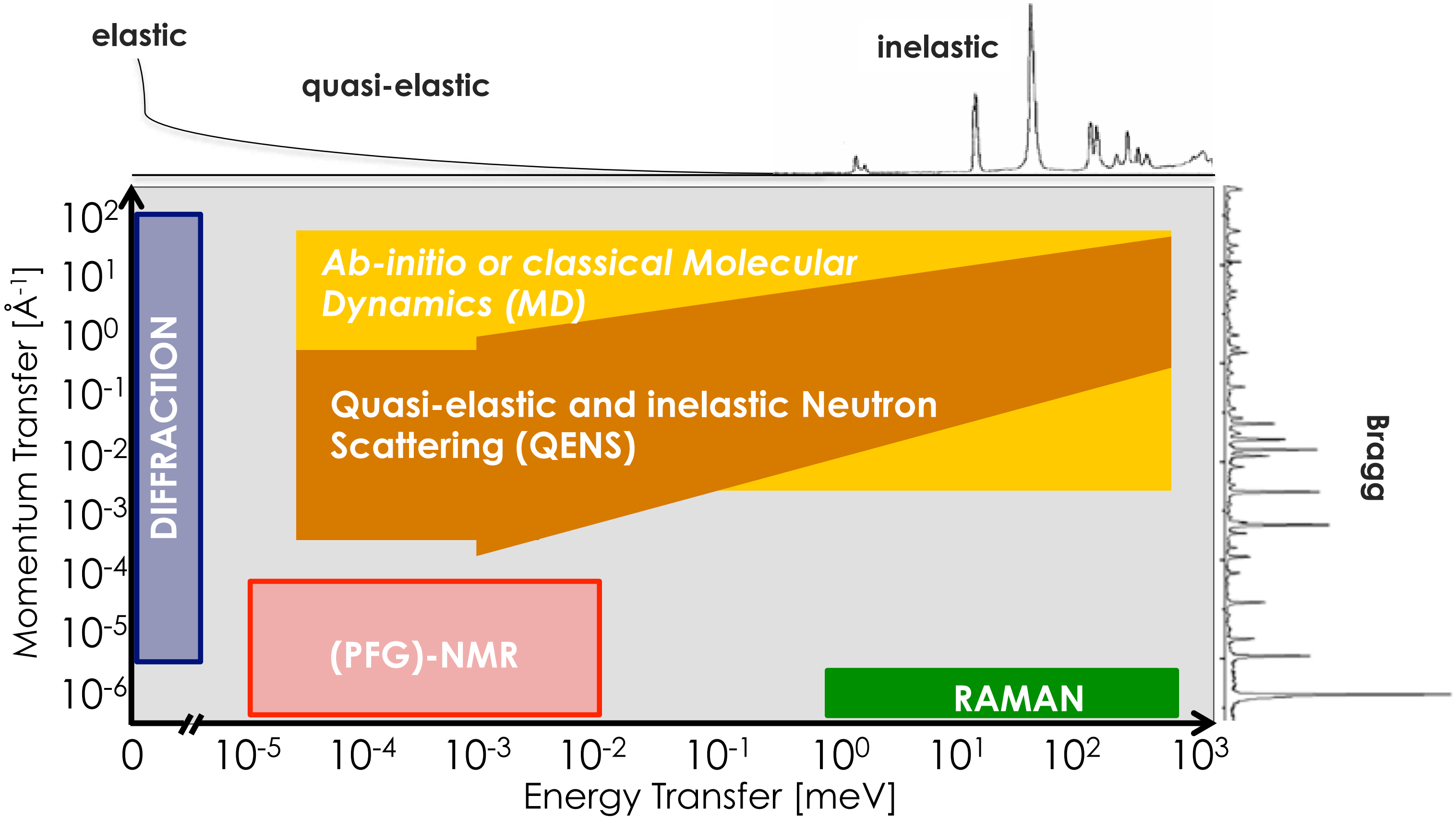
Methodology



Source: Forschung mit Neutronen - Status und Perspektiven, KFN

✓ Combining spectroscopy and simulations

Combining experiments and simulations.



✓ **Raman: HP-BT optical set-up + in-situ measurements**

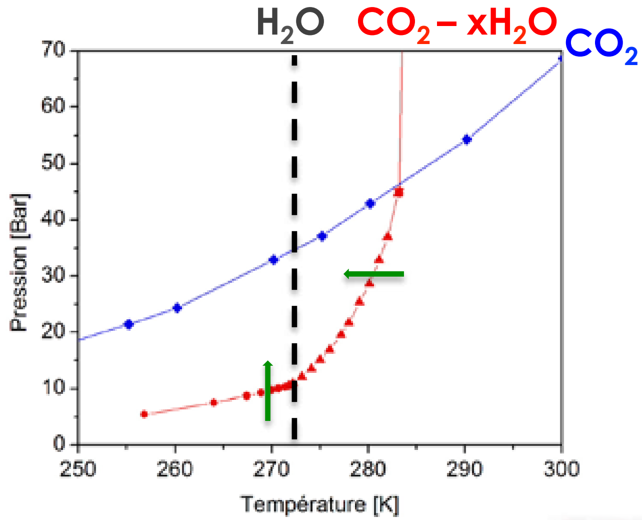
✓ **MD/QENS: common observables**

e.g. A. Desmedt *et al*, *J.Phys.Chem.C*, **115(26)**, 12689 (2011) // E. Pefoute et al,

✓ **Ab-Initio MD: one of the simplest way for "reactive" MD**

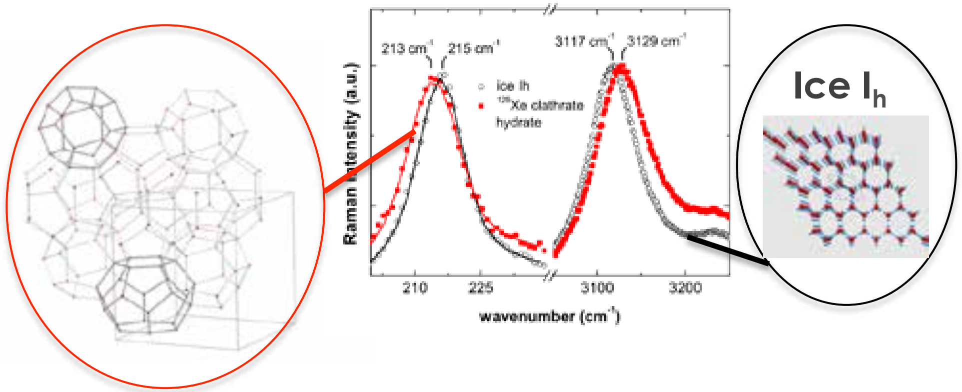
e.g. L. Bedouret, PhD Univ. Bordeaux, 2013

Gas hydrate: in-situ Confocal Raman microspectrometry



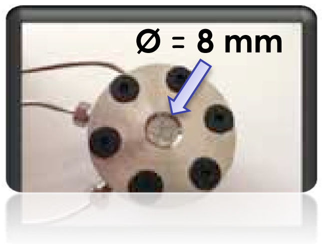
✓ **e.g. Xenon clathrate hydrate (type I)*** @150K/1bar

*B. Klobes, *et al*, *EPL* **103** (2013) 36001



Synthesis

In-situ Raman



Raman spectra and imaging with *µm* spatial resolution

- HJY "HR evolution" confocal microspectrometer with excitation wavelengths:
325, 458, 488, 514, 633, 752, 1064 nm
- Gas pressure range from **1 to 250bars**
- Temperature range from **150K to 300K**
- Pressure device for preparing gas mixture
- 2mm Sapphire optical window; ½ **cm^3 sample**

Lab-made optical stage for microscopy

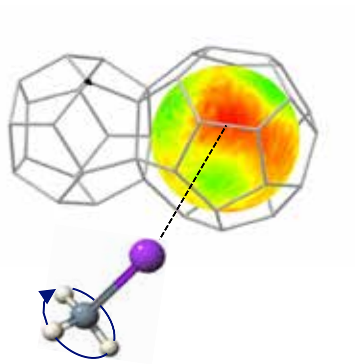
"Ab-initio" and classical molecular dynamics?

▶ **How to treat the proton transfer in H-bond: $H_3O^+ + H_2O \rightarrow H_2O + H_3O^+$?**

Classical Molecular Dynamics (MD)	**"*Ab-initio*" Molecular Dynamics (AIMD)**
Potential energy: force field	*On the fly potential energy: Born-Oppenheimer + DFT*
$U(r) = \sum_{paires}\left[\sum_{\alpha\in A}\sum_{\beta\in B} 4\varepsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}}\right)^{6}\right] + \frac{q_\alpha q_\beta}{r_{\alpha\beta}}\right]$	$H\left\|\psi_n\right\rangle = \epsilon_n \left\|\psi_n\right\rangle$
⬇	⬇
Newton's equation of motion (nuclei)	*Newton's equation of motion (nuclei)*
⬇	⬇
Trajectories	*Trajectories*
• large systems (more than 1000 atoms) • duration: several 10ns with ~10fs timestep	• « smaller » systems (less than 1000 atoms) • duration: 500ps with fs timestep

Classical MD and Quasi-elastic Neutron Scattering (QENS)

▶ **example of the methyl iodide clathrate hydrate**

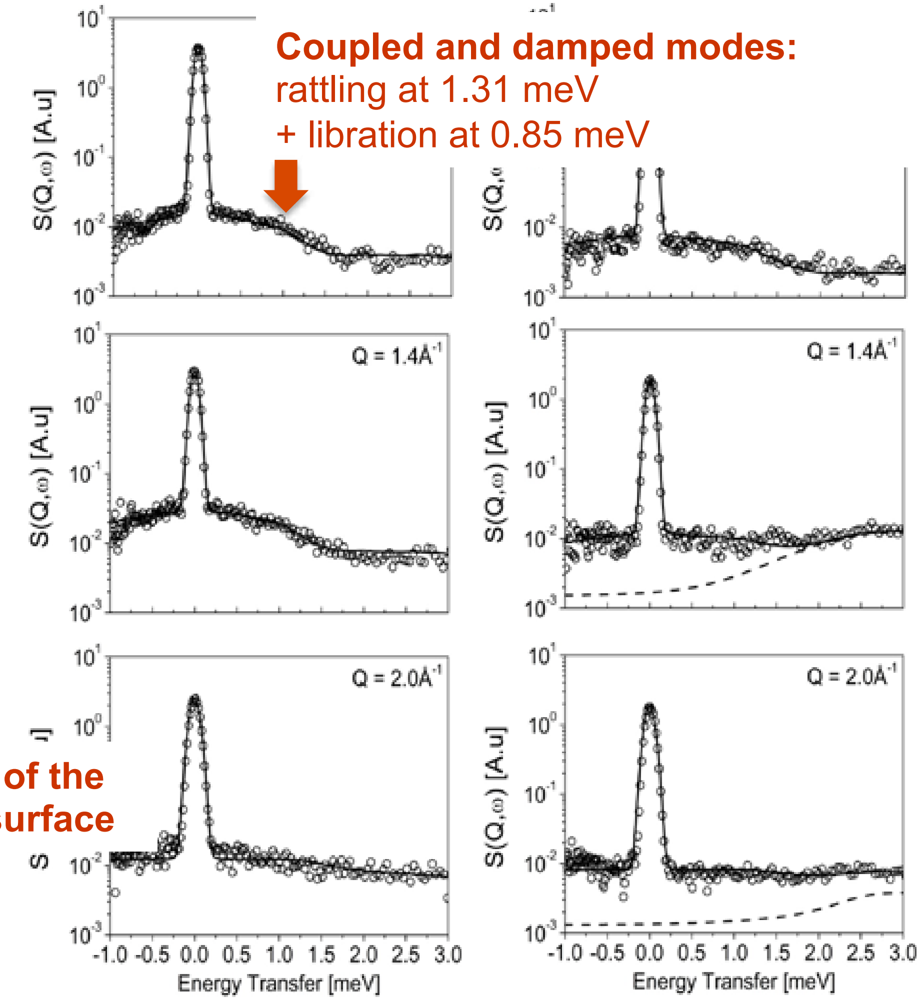


CH_3I – 17D_2O (type II)

Existence of adsorption sites of the guest molecules at the cage surface

T = 150K **T = 270K**

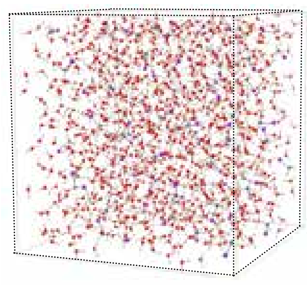
Coupled and damped modes:
rattling at 1.31 meV
+ libration at 0.85 meV



○ **QENS**

NEAT@HZB, Berlin
$\Delta E \approx 100\mu eV$
$\lambda_0 = 5.1Å$

— **MD**

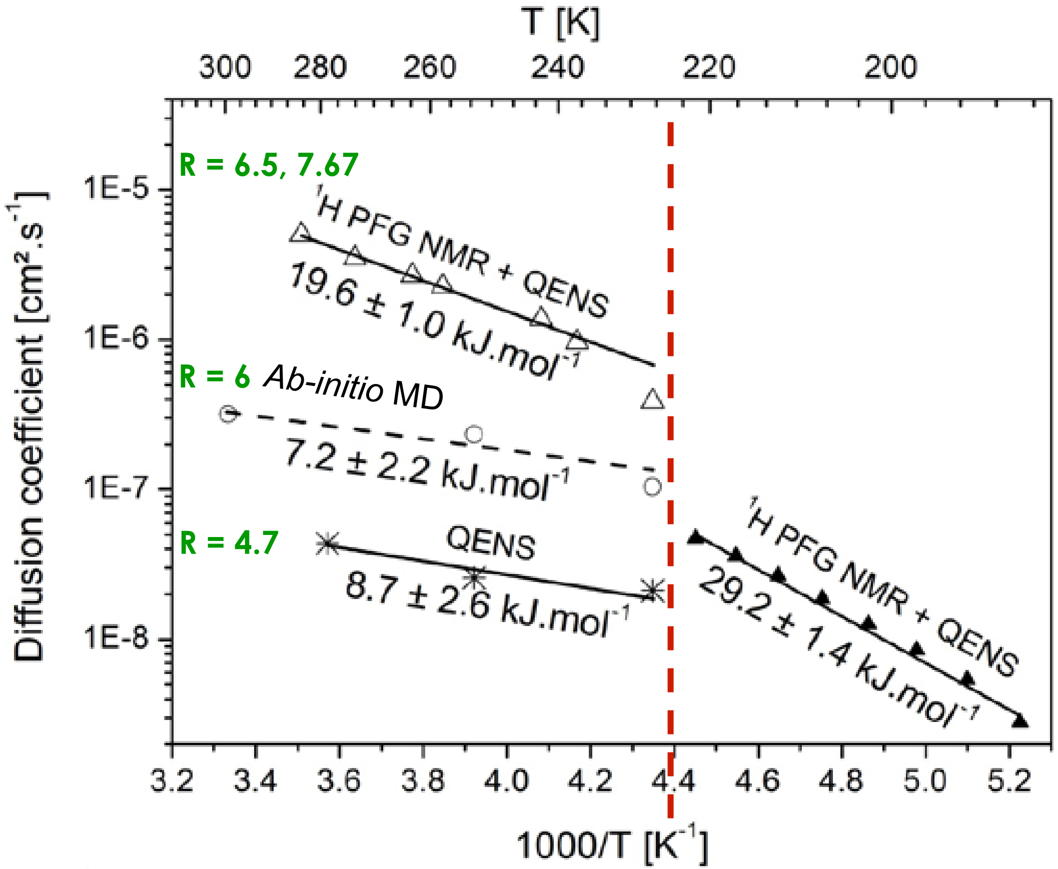


2 x 2 x 2 type II Unit
SPC/E for water
Ab-initio for guest
NVE ensemble
2 ns MD length

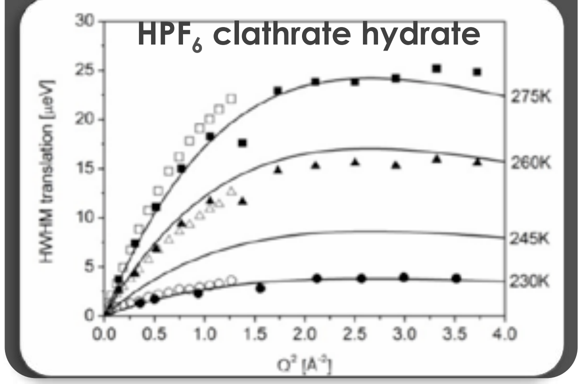
A. Desmedt *et al*, *J.Phys.Chem.C*, **115(26)**, 12689 (2011)

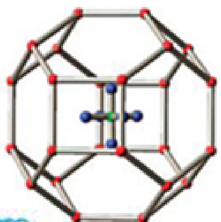
Long-range proton diffusion in strong acid clathrate hydrates

▶ **Combining QENS, ^{1}H PFG-NMR and *AI*MD**



<u>Mechanism (QENS HWHM)</u>:
Proton jump diffusion between oxygen sites



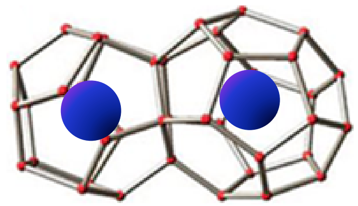


HPF_6 – RH_2O(type VII)

Conductivity measurements*
E_A = 9.6 kJ.mol^{-1}

$HClO_4$ – $5.5H_2O$ (type I)

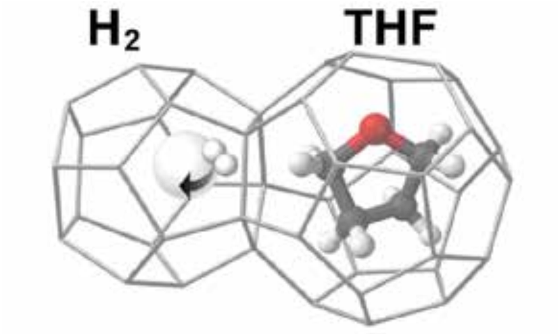
Conductivity measurements †
E_A = 33.7 kJ.mol^{-1}



*J.H. Cha *et al*, J. Phys. Chem C **112**,13332 (2008) // † T.-H. Huang et al, *J. Phys. Chem*. **92** (1988) 6874

L. Bedouret *et al, J. Phys. Chem. B 118 (2014) 13357−13364*// A. Desmedt *et al* J. Chem. Phys., **121**, 11916 (2004)

Hydrogen diffusion in the THF-H_2 clathrate hydrate



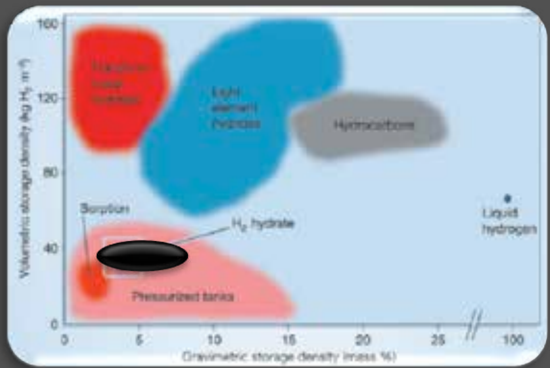
- ✓ Mechanism of inter-cage diffusion of hydrogen?
- ✓ Impact of acidic defects onto hydrogen insertion?

Hydrogen storage in clathrate hydrates?

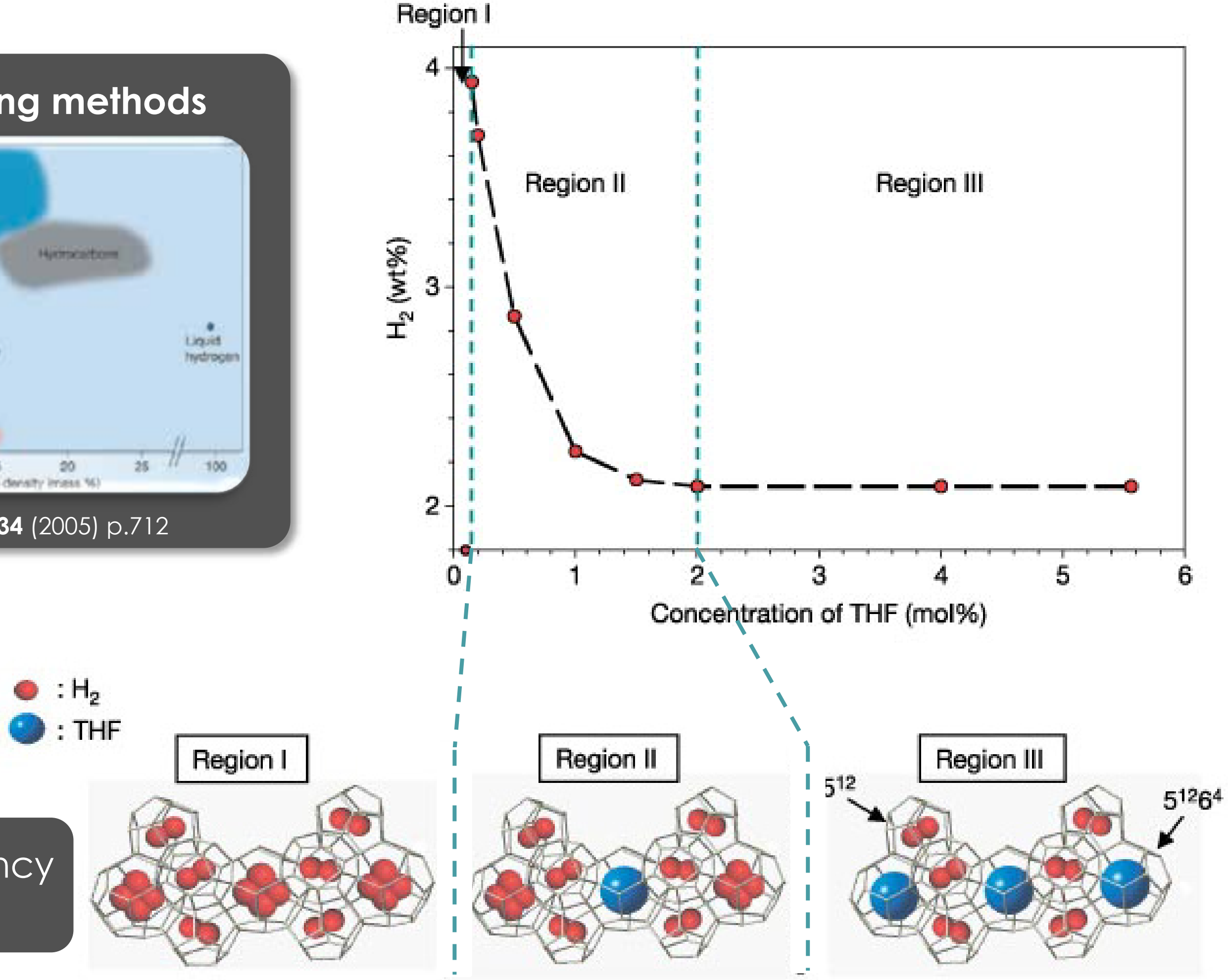
✓ **Softening H storage conditions:**

from pure H_2 to binary H_2-tetrahydrofuran (THF) clathrate hydrate

✓ **Various storing methods**



F. Schüth, *Nature* **434** (2005) p.712



No multiple occupancy of small cages!

P ~ 2000 bars, T = 273K

Pure H_2 hydrate ⇔ 5wt% H_2

Y.A. Dyadin, *et al*, Mendeleev Commun. **9** (1999) p.209

L. Mao *et al, Science* **297** (2002) p.2247

P = 70 bars, T = 277K

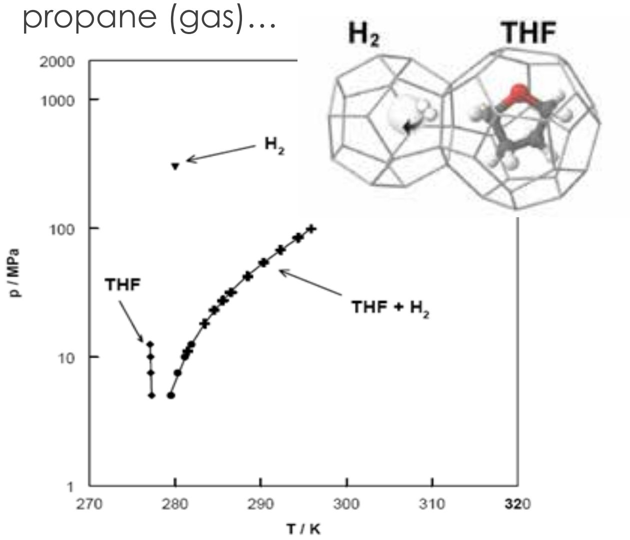
L.J. Florusse, *et al*, Science **306** (2004) p.469

H. Lee *et al*, *Nature* **434** (2005) p.743

Co-including various chemical species?

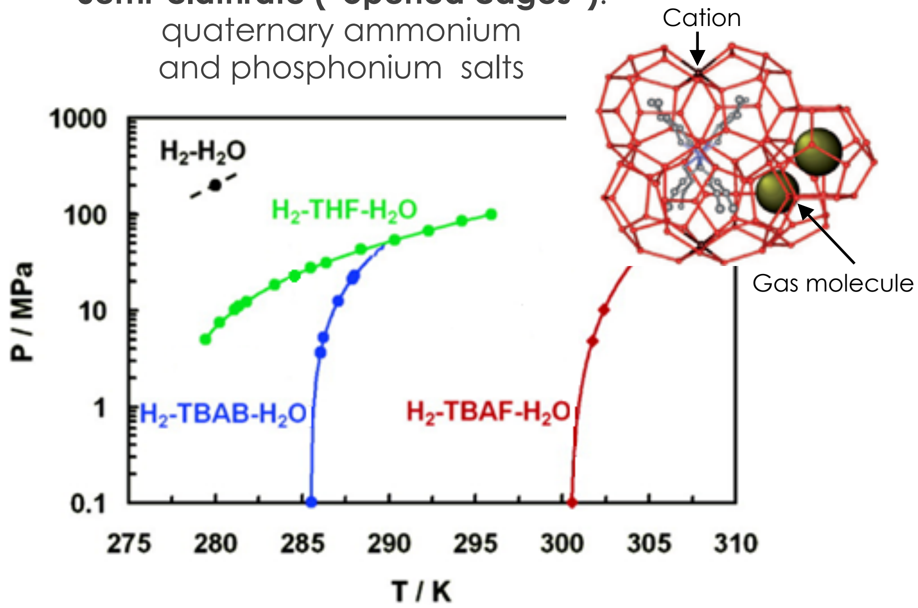
✓ **Various thermodynamics promoters (SI, SII, SH, SVI, semi-clathrate, etc…)**

- **Type II structure:** THF, cyclopentane, cyclohexanone, furan (liquid),.. propane (gas)…

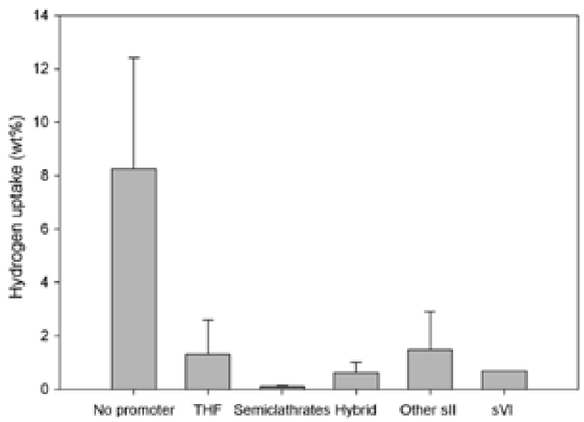


L.J. Florusse, *et al*, Science **306** (2004) p.469

- **Semi-clathrate ("opened cages")**: quaternary ammonium and phosphonium salts



A. Chapoy, *et al*, JACS **129** (2007) p.746



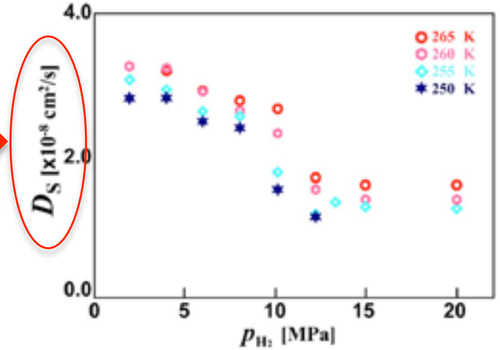
H.P. Veluswamy et al., Applied Energy **122** (2014) 112–132

Limited storage capacities….
…but fundamentally interesting.

Hydrogen diffusion through water cages at various P-T

^{1}H PFG-NMR measurements

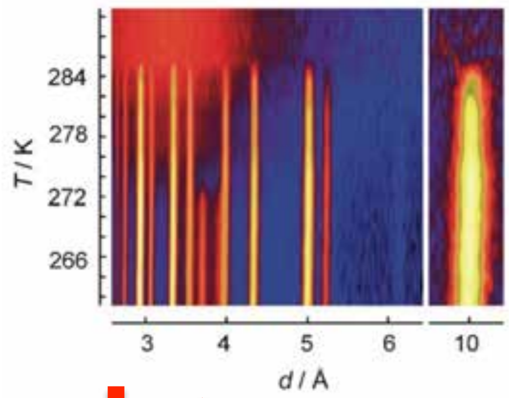
T. Okuchi *et al.*, Appl. Phys. Lett. **91** (2007) 171903



Different ^{1}H PFG-NMR analysis: no diffusion observed.

L Senadheera, *et al*, J. Phys. Chem. B 112 (2008) 13695.

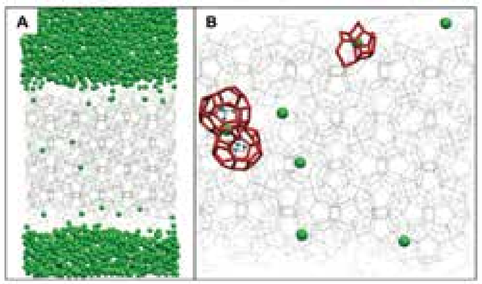
In situ neutron diffraction



D~10^{-11} cm^2/s at 90bar and 264K

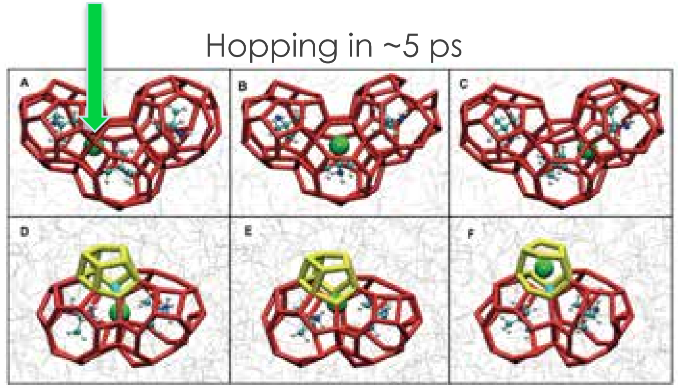
➔ Various measurements leading to a wide range of H_2 diffusion coefficient

MD simulations of hydrogen / tert-butylamine ($tBuNH_2$) sVI clathrate hydrate **at 230K and 850bars**



Interstitial residence time ~10-20ns
(assuming isotropic ~1nm jump diffusion ~10^{-7} cm^2/s)

Hopping in ~5 ps

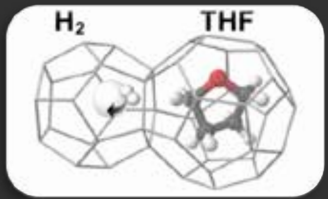


R.G. Grim *et al.*, Angew. Chem. Int. Ed., **53** (2014) p.10710

➔ Interstitial H_2 positions recently evidenced

Dynamics of H_2 confined within a water cage at 1 bar

✓ **Exploring H_2 dynamics by means of Quasielastic Neutron Scattering and Raman Scattering**

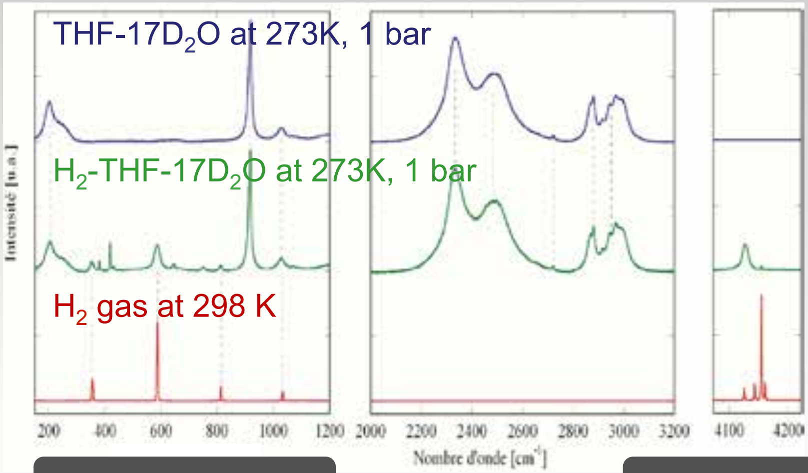


Type II clathrate-hydrate **C_4D_8O - H_2 / $17D_2O$:**
H_2 pressure onto THF clathrate hydrate powder sample

⇨cage occupancy (pressure release measurements)
= 0.74 after 1 week at P = 300bars (QENS)
= 0.11 after 1 day at P = 190bars (Raman)

$$S_{H2}(Q,\omega) = \underline{S_{rotation}(Q,\omega) \otimes S_{vibration}(Q,\omega)} \otimes \mathbf{S_{translation}(Q,\omega)}$$

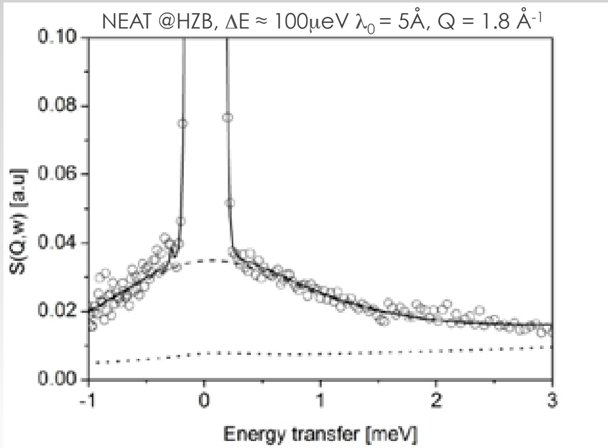
Raman Scattering



H_2 rotons

H_2 vibrons

Incoherent Quasielastic Neutron Scattering (250K, 1bar)

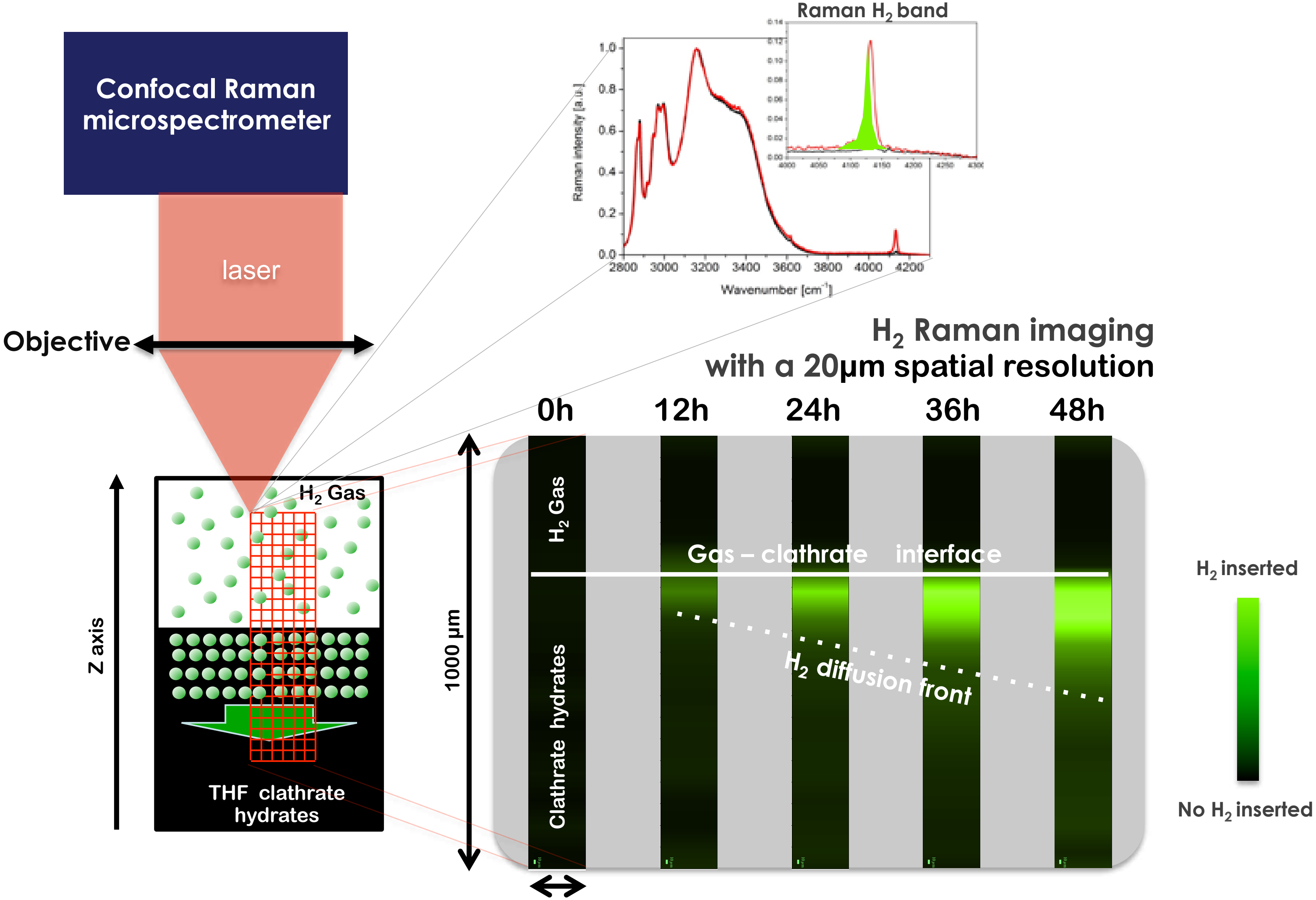


E. Pefoute *et al*, *J.Phys.Chem.C* **116**, 16823 (2012)

Localized diffusion within the cage (no H_2 inter-cage diffusion)

H_2 insertion mechanism?

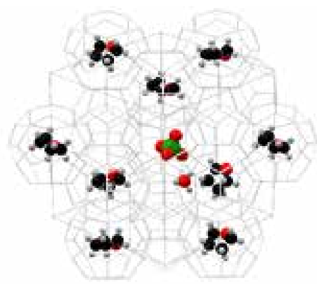
✓ *In-situ* Raman imaging of H_2 insertion within *THF · 0.125 HClO$_4$ · 17 H$_2$O* clathrate hydrate (H_2 pressure = 200bars at 270K)

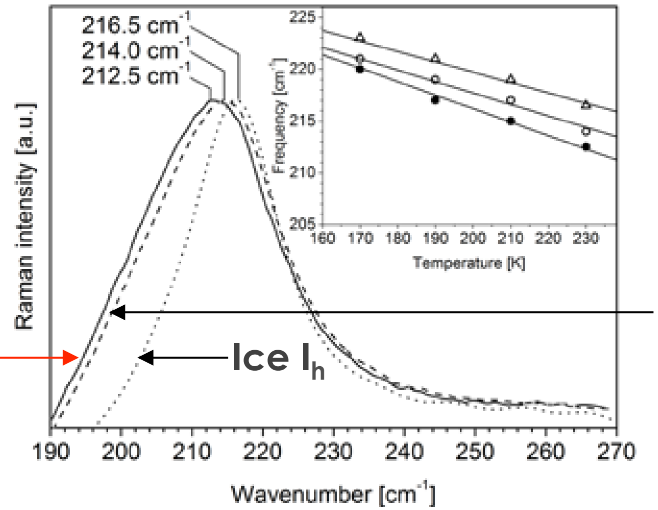


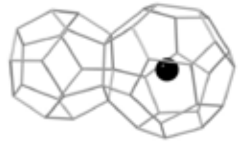
T.T. Nguyen *et al*, in preparation

Impact of perchlorate anion encapsulation.

- **“Cage” phonon of the type II clathrate hydrates *THF · 0.125 HClO$_4$ · 17 H$_2$O* at 150K**

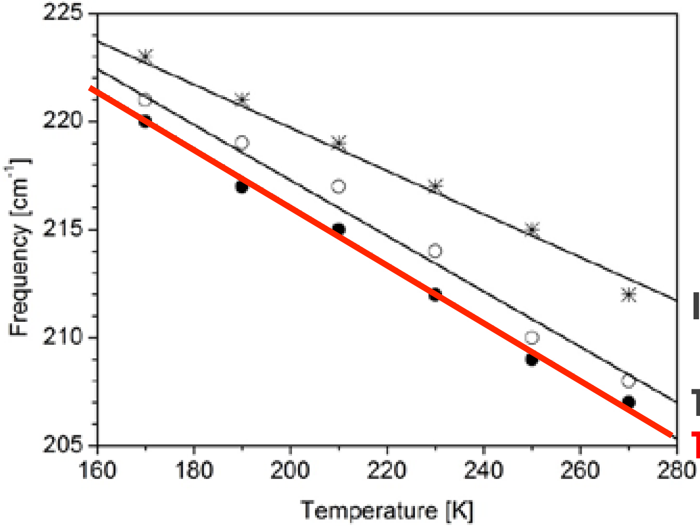






THF hydrate with acid

THF hydrate without acid



Ice I$_h$

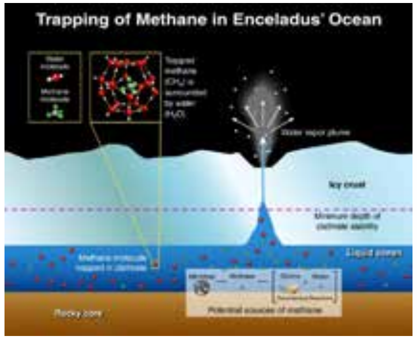
THF hydrate without acid

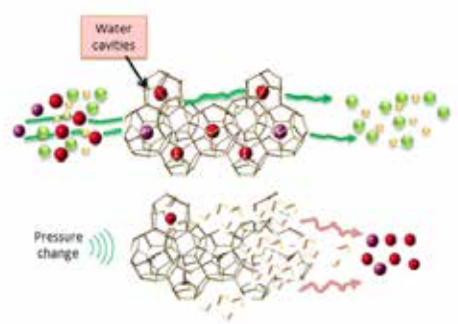
THF hydrate with acid

⇨ Impact of acidic additives: softening of the cage phonon

A. Desmedt *et al*, J. Phys. Chem B, **119 (16)**, 8904 (2015)

Selectivity in the CO-N_2 clathrate hydrate





- ✓ Experimental investigations
- ✓ Driving factors at molecular scale?

Selectivity in clathrate hydrates

Examples of driving factors

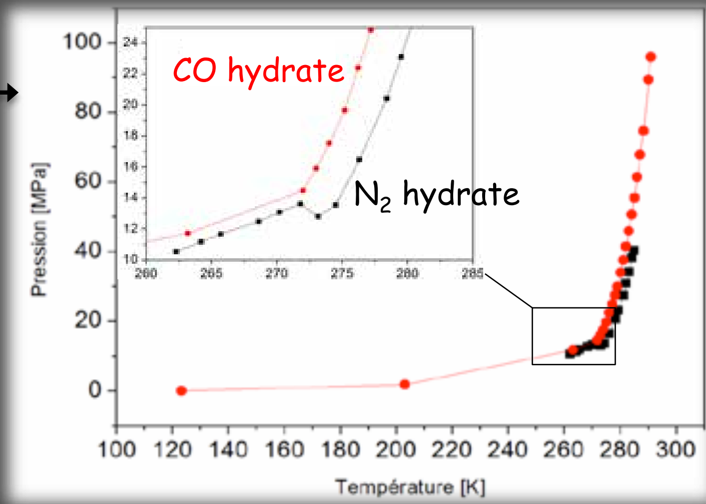
- Steric hindrance
- Thermodynamic conditions of formation
- Physico-chemistry of the guest molecule (water solubility, dipolar moment …)

Mixed CO – N_2 clathrate hydrate?

- Similar size — C≡O 112,8 pm; N≡N 109.76 pm
- Similar phase diagrams
- **Different dipolar moment**
- Well appropriated for **combined theoretical AND experimental approach.**
- **Relevant for astrophysics** (predominant form of N and C)

67P/Tchourioumov Guérassimenko

Phase diagrams of the pure clathrate hydrates

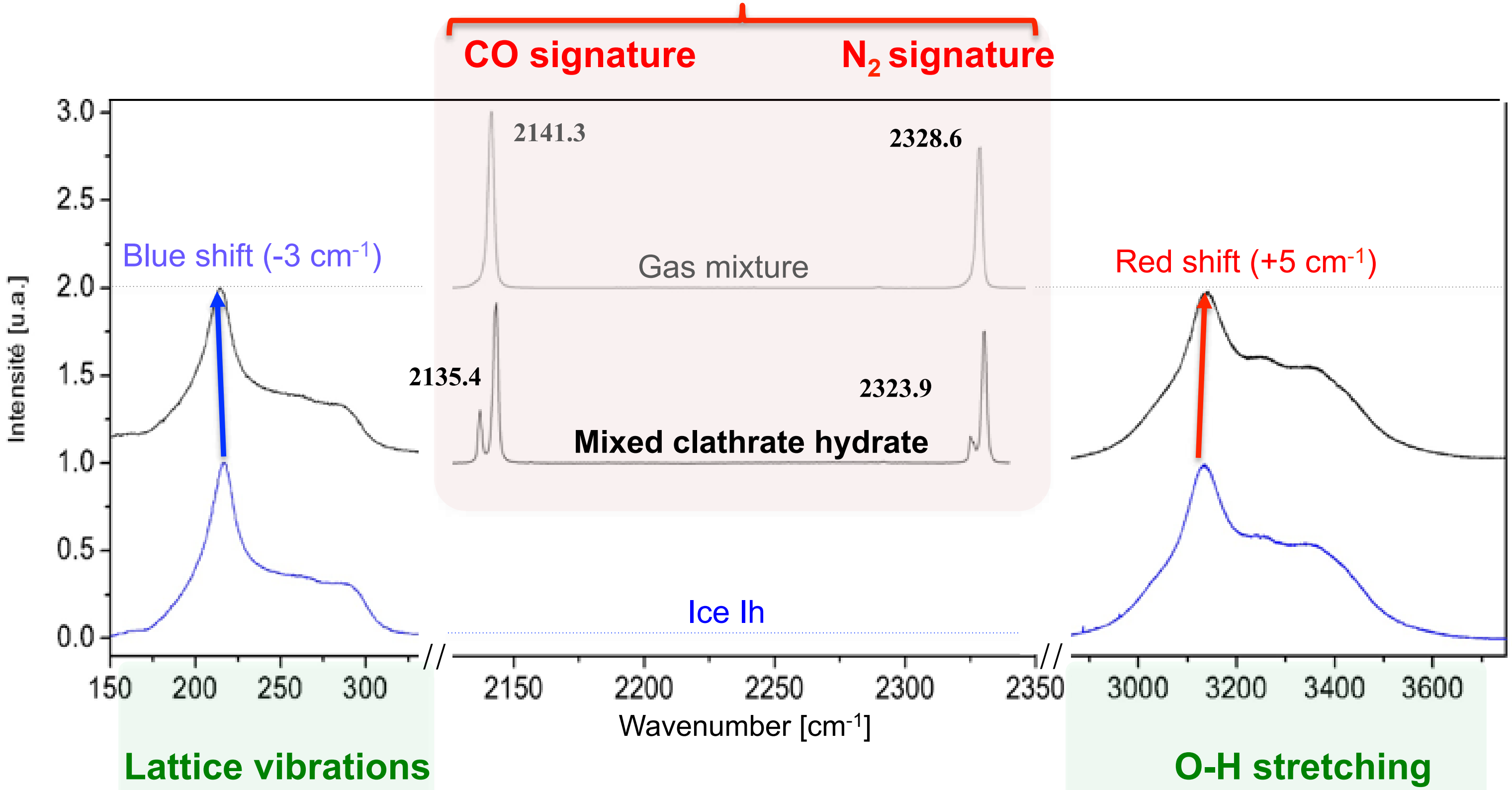


Mohammadi A.H. *et al*, *Ind. Eng. Chem. Res.*, **2010**, 49, 3976
Sun Q. *et al*, *Fluid Phase Equilibria*, **2011**, 307, 95,

Raman spectra of the mixed clathrate hydrate

- **Mixed clathrate hydrate prepared by applying a 50% CO / 50% N_2 gas mixture onto ice at 250K and 150 bar**

Guest signatures with respect to gas: encapsulation
⇨ Blue shift: confinement effect
⇨ Modification of CO/N_2 intensity ratio in hydrate phase with respect to gas phase

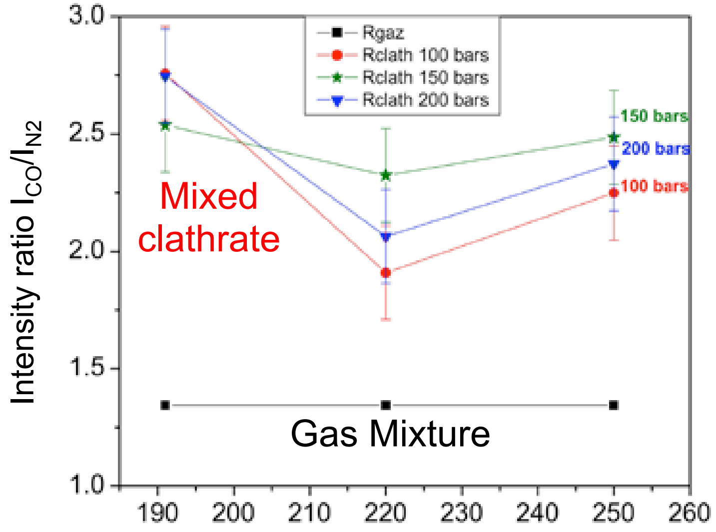


Water signatures with respect to ice: formation of water cages
⇨ Blue shift of the lattice modes: distortion of the H-bond network
⇨ Red shift of the OH stretching: strengthened O-H bonds

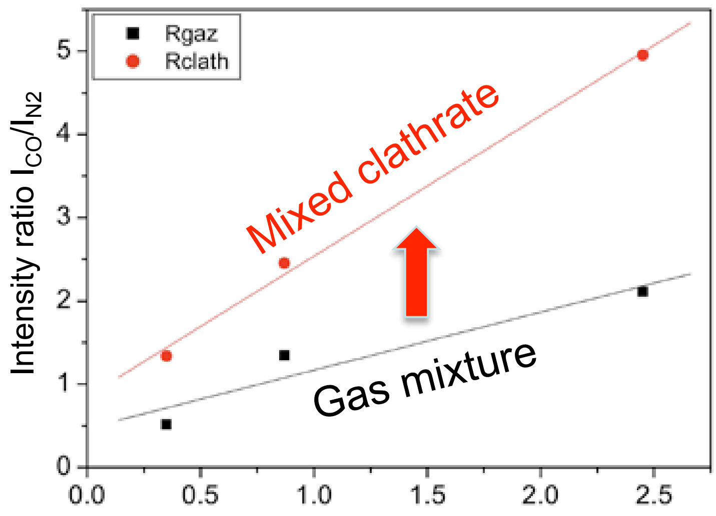
Investigating the selectivity by Raman spectroscopy

▶ **Analysis of the intensity ratio of CO to N_2 stretching modes for:**
- Various gas mixture composition
- Various (P,T) conditions

Ratio for 50% CO / 50% N_2 gas mixture



Ratio averaged over T-P



Raman intensity depends on (not only):
- the polarisability's variation
- the molecular concentration

$$R_X = \frac{I_{CO_X}}{I_{N2_X}} = \frac{[CO]_X}{[N_2]_X}\left(\frac{\alpha'_{CO_X}}{\alpha'_{N2_X}}\right)^2$$

X refers to gas or clathrate

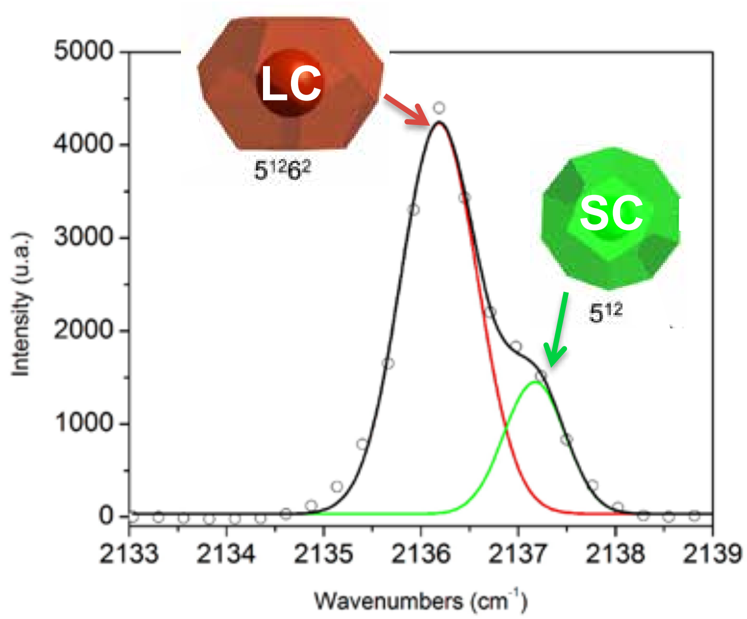
Preferential encapsulation of CO whatever the chemical composition and (P,T) conditions are

C. Petuya *et al*, in preparation

Filling of the cages?

▶ **Cage occupancy in the CO clathrate hydrate (type I)**

High-resolution Raman
at T = 190 K and P = 200 bar



Quantum calculations of vibration frequencies
in the DFT approximation

VASP calculations details:

- periodic boundary conditions, PAW, GGA
- exchange-correlation functional PBE
- Simulation box type I : 46 H2O + 8 guest molecules (a=12Å)
- Structural Relaxation (cell parameter and potential energy)
- Frequency calculations: harmonic approximation+ rigid H_2O

TYPE I		GAS
ν LC [cm^{-1}]	ν SC [cm^{-1}]	ν [cm^{-1}]
2150	2157	2141

- **Relative values of frequencies in excellent agreement with experiments**
- **Absolute values: correction for anharmoncity?**

C. Petuya *et al*, in preparation

Concluding remarks

⇨ **Hydrogen diffusion:**

- *Proposed H_2 diffusion mechanism (Fick diffusion), i.e 2 H_2 molecules may meet in a single cage!*
- Adding acid to THF clathrate hydrate = *enhancing of the H_2 up-take kinetics*

⇨ **Molecular selectivity:**

- *CO-N_2 mixed clathrate hydrate: a clear experimental evidence of preferential CO encapsulation.*
- *Role of the guest dipolar moment CO vs N_2 ?*
- *Cage occupancy? Formed structure?*
- *Contribute to the understanding of cometary and planetary compositions?*

⇨ **Combined experimental and modelling approach:**

- *Raman scattering: a very sensitive microscope for in-situ measurements.*
- *DFT calculations: required tool for interpretation.*

⇨ **Perspectives:**

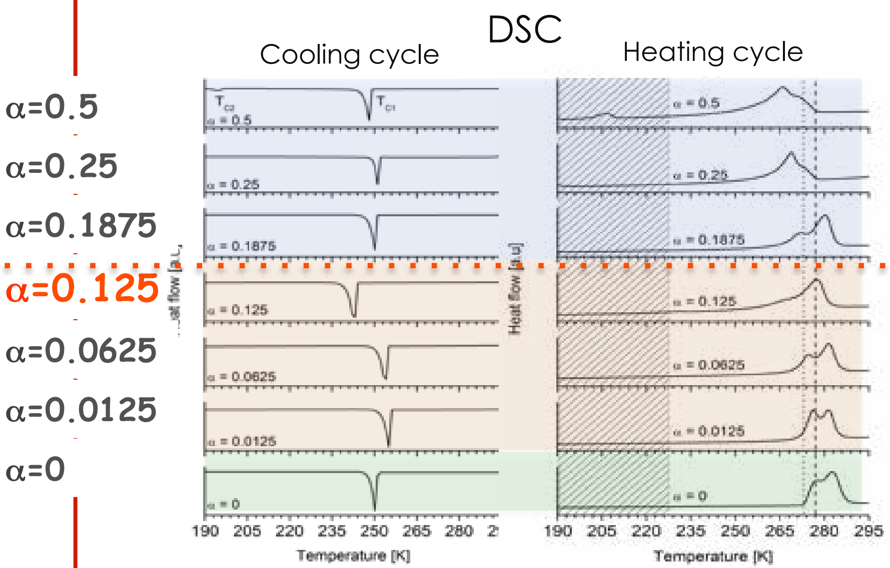
- *Impact of sediments onto molecular selectivity?* ***ANR MI2C***

THANK YOU FOR YOUR ATTENTION!

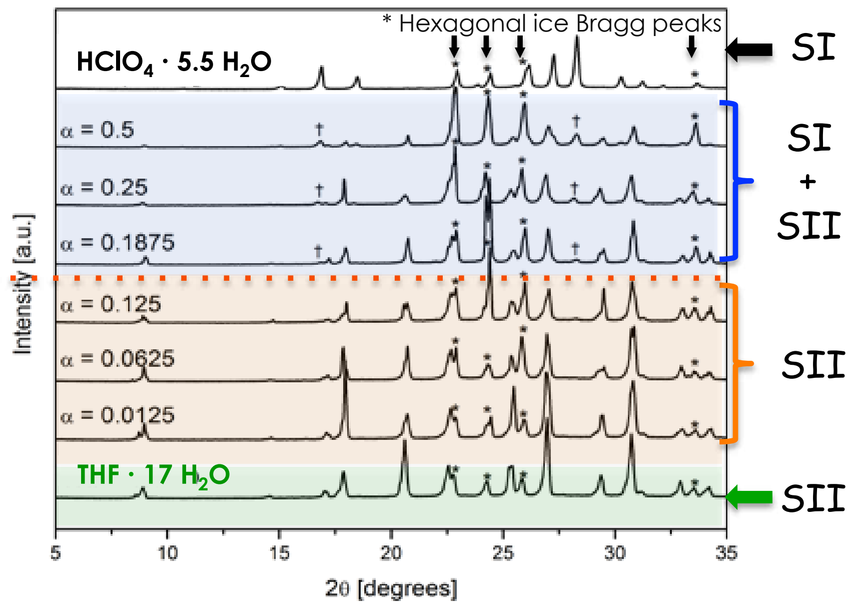
Structure and thermodynamics.

▶ **Powder X-ray diffraction and Differential Scanning Calorimetry**

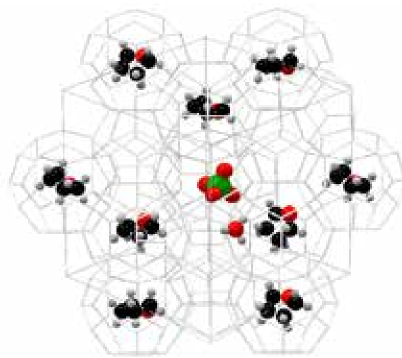
Clathrate hydrate (1-α) THF · α $HClO_4$ · 17 H_2O



PXRD at 150K



- ✓ For α > 0.125: multiphasic clathrate (SI+SII)
- ✓ For α ≤ 0.125: a single clathrate phase SII

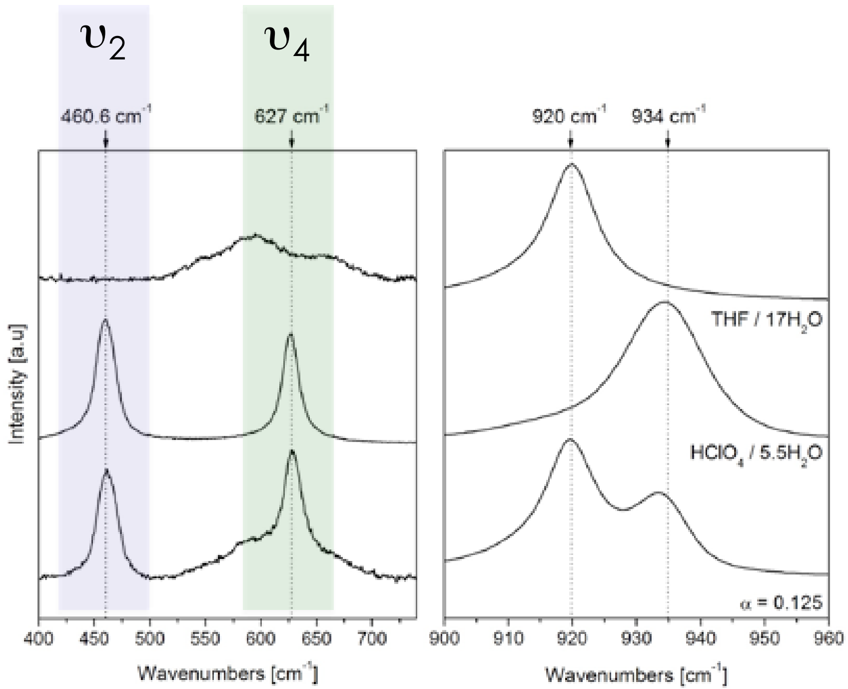


A. Desmedt *et al*, J. Phys. Chem B, **119 (16)**, 8904 (2015)

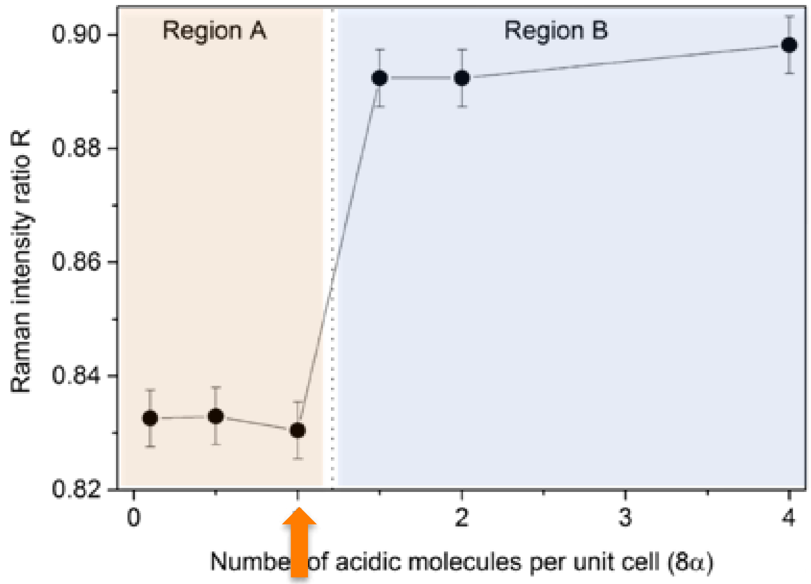
Signature of perchlorate anion encapsulation.

- **Raman scattering**

Intensity ratio R = $I(\upsilon_4)/I(\upsilon_2)$ **for $HClO_4 \cdot 5.5\ H_2O$:** **- acidic solution (T > 228K)**: R = **0.95**
- type I clathrate (T < 228K): R = **0.32**



Clathrate hydrate (1-α) THF $\cdot$ α $HClO_4 \cdot 17\ H_2O$



α = 0.125

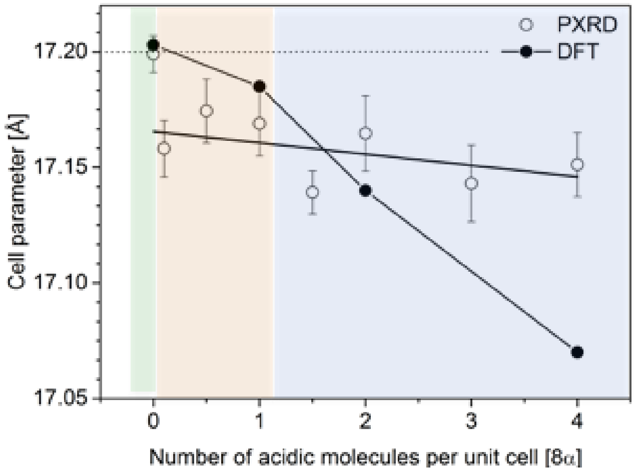
Inherent limit of acid concentration corresponds to 1 acid per unit cell

A. Desmedt *et al,* J. Phys. Chem B, **119 (16)**, 8904 (2015)

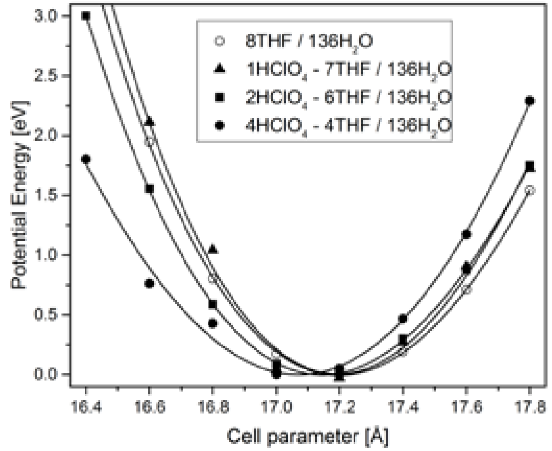
Impact of perchlorate anion encapsulation.

▶ **Cell parameters by means of PXRD and DFT structure relaxation**

Clathrate hydrate (1-α) THF · α $HClO_4$ · 17 H_2O



Birch-Murnaghan equation of state



⇨ shrinkage of the unit cell

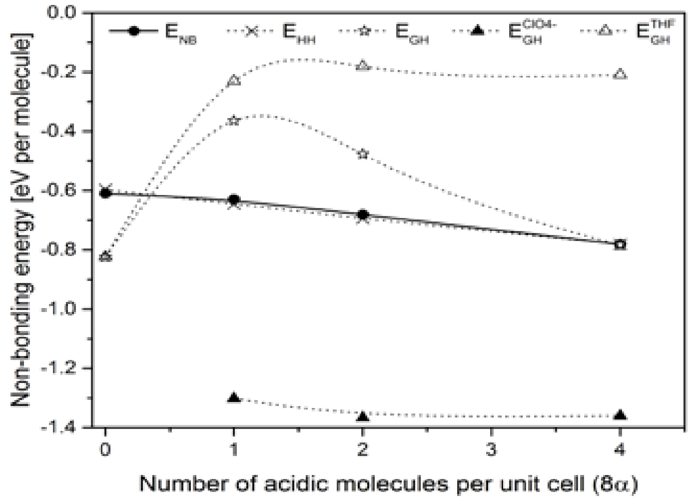
▶ **Non-binding energy (**molecular interactions**)**

$$E_{NB} = (E_c - N_h E_h - N_g E_g)/(N_h + N_g)$$

$$E_{NB} = (N_h E_{HH} + N_g E_{GH})/(N_h + N_g)$$

$$\text{with } E_{HH} = (E_{ec} - N_h E_h)/N_h,$$

$$\text{and } E_{GH} = (E_c - E_{ec} - N_g E_g)/N_g$$



⇨ stabilizing the clathrate

A. Desmedt *et al,* J. Phys. Chem B, **119 (16)**, 8904 (2015)