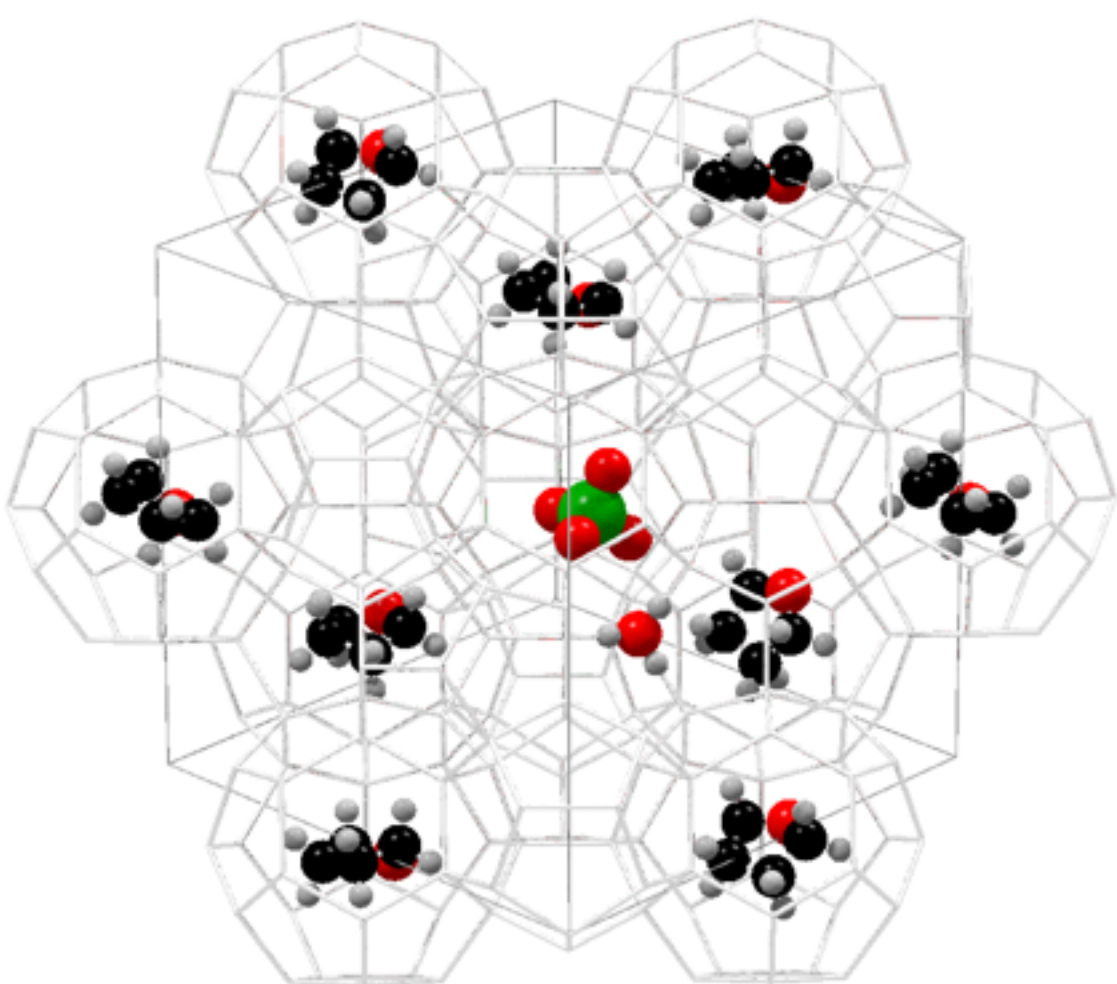
COLLOQUIA 12-2019

NEUTRONS FOR SCIENCE



PHYSICAL-CHEMISTRY OF GAS HYDRATES : FROM ASTRO- / GEO- PHYSICS TO NEW OPPORTUNITIES FOR ENERGY TECHNOLOGIES.

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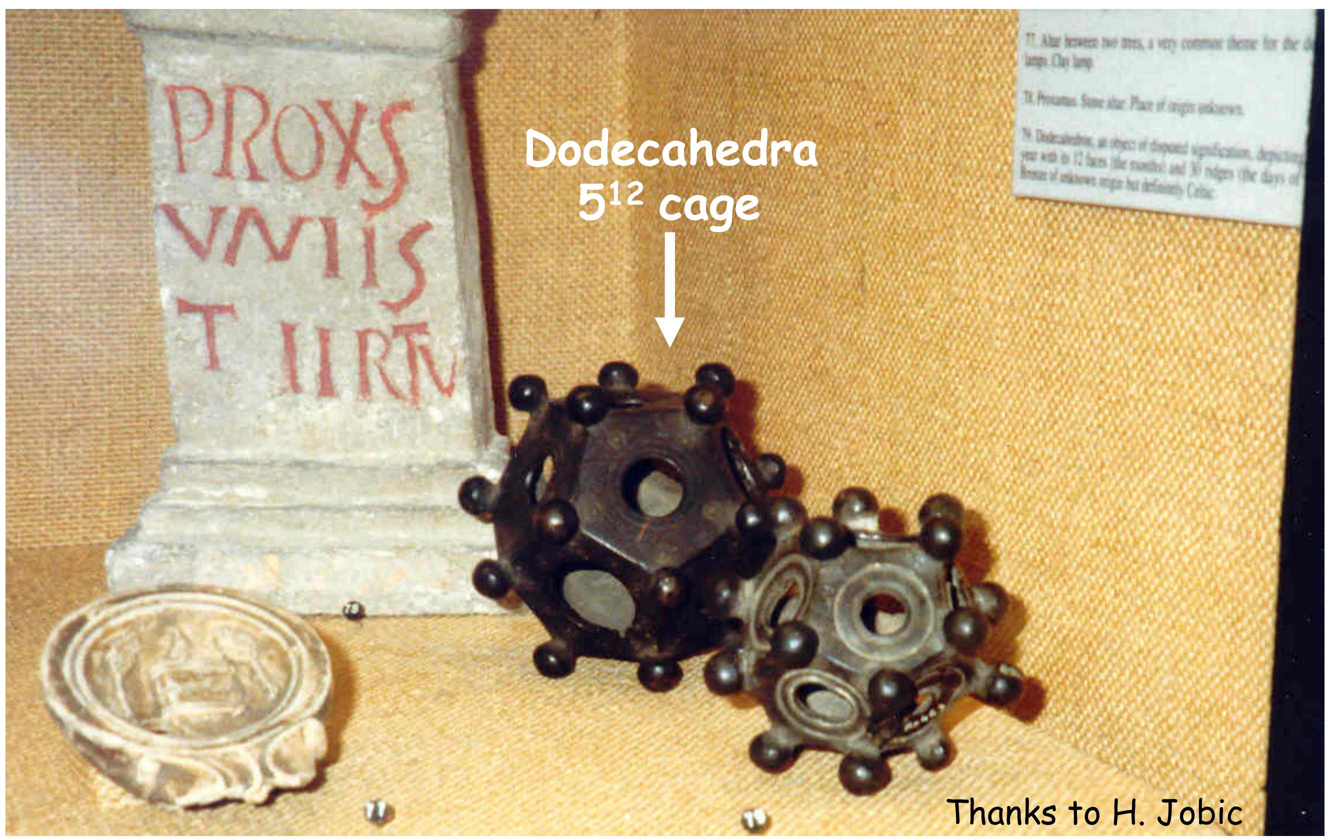
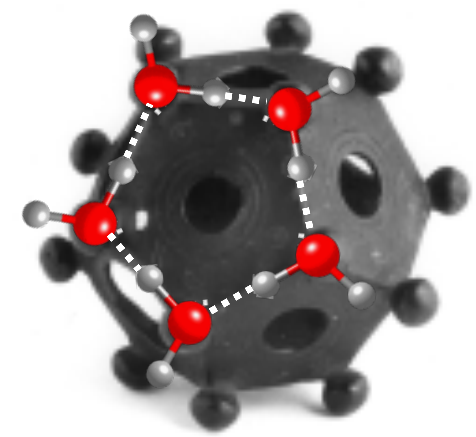
INTRODUCTION

A CORRECTION TO THE HISTORY…

"Musée Gallo-Romain de Lyon"

"objects of disputed signification but definitely of **Celtic origin**"





The first model for hydrate is more than 2000 years old?

STRUCTURES

- Cages constituted of water molecules + encapsulated guest

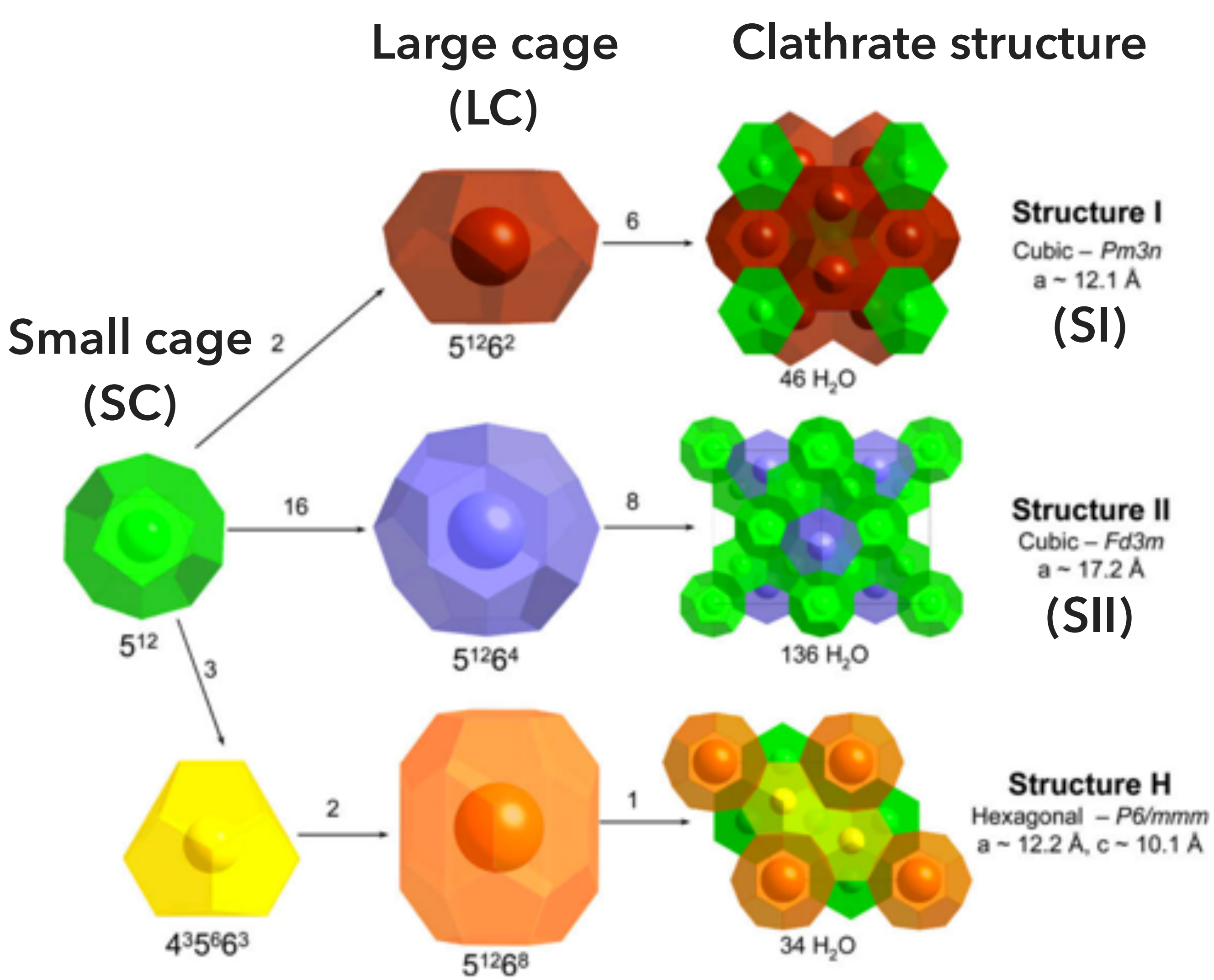
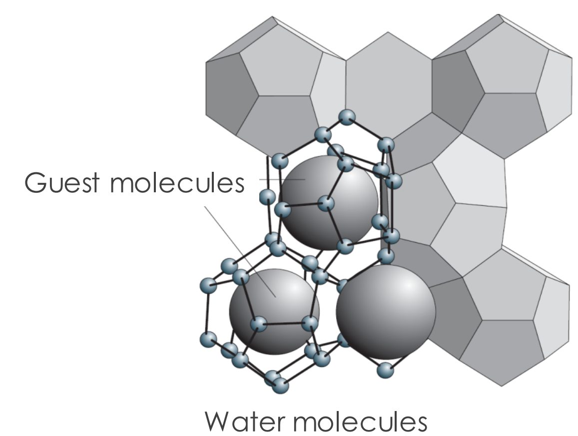


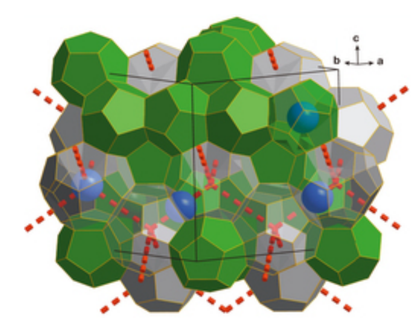
Fig. 1. Common clathrate hydrate structures.

Strobel et al, Chem. Phys. Letter, 2009



Stable only with guests ?

…Ice phase XVI: clathrate with empty cages

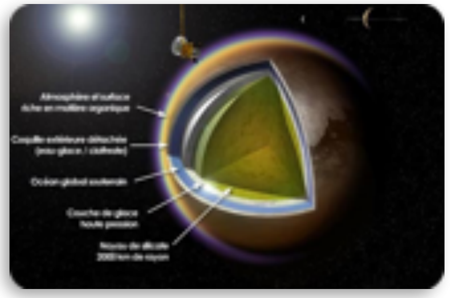


Neutron Diffraction onto vacuum-pumped neon clathrate hydrate.
A. Falenty, *et al*, Nature 516, 231–233 (2014)

CONTEXT

Energy reservoir

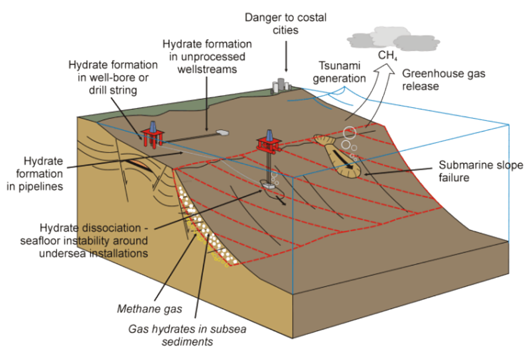
Existence?

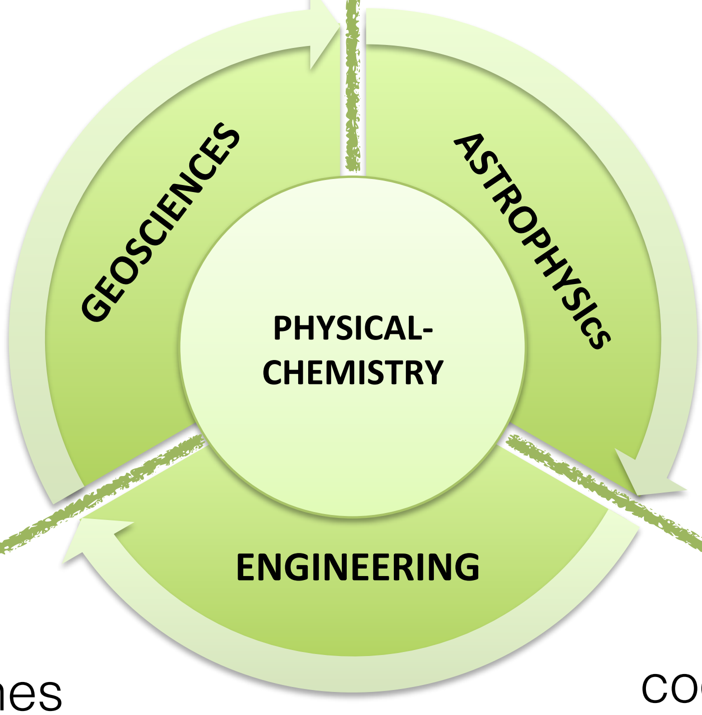


geohazard

climat

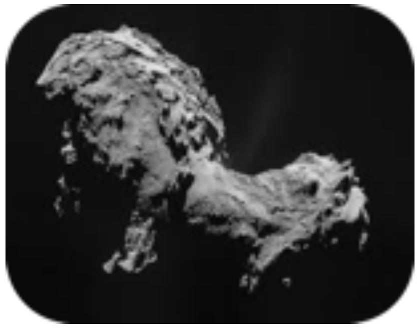
CO_2 sequestration





planet, comet formation

atmosphere

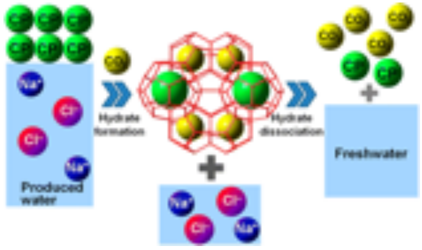


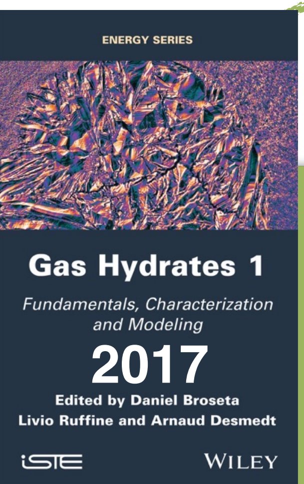
pipelines

cooling

gas separation

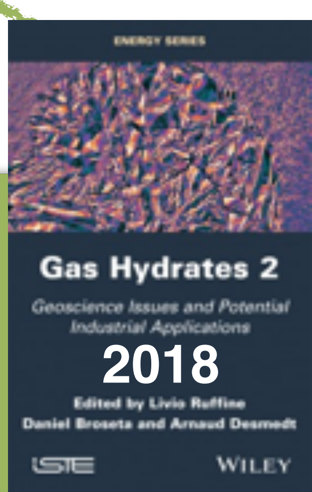
desalination





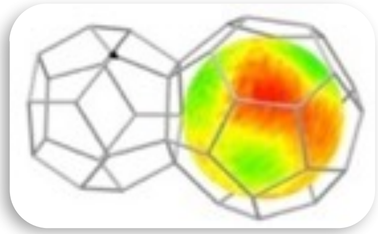
Fundamentals: physical-chemistry

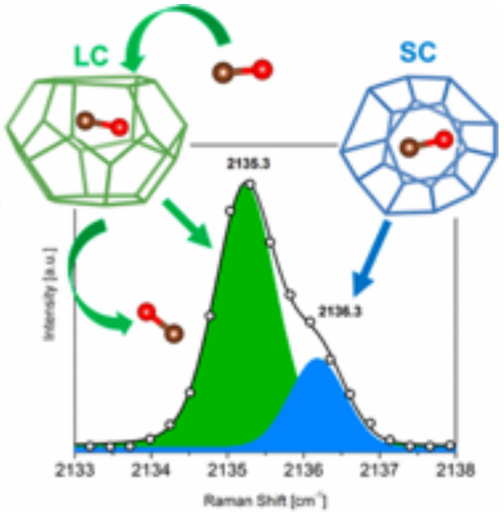
- organisation and dynamics
- chemical composition
- (meta-)stability
- formation mechanism
- transport/diffusion
- hydrate/substrates interface



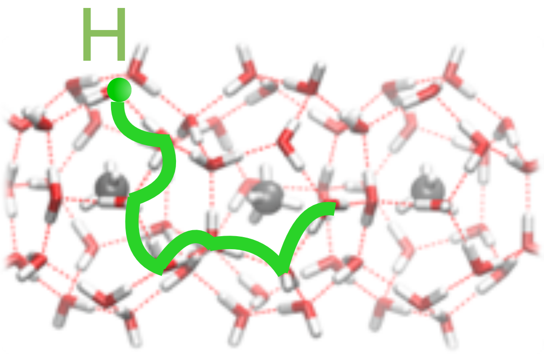
OUTLINES

- METHODOLOGY:
  illustrating neutron scattering contributions





- GAS HYDRATES:
  Metastability, cage occupancy, molecular selectivity
  …towards natural gas hydrates

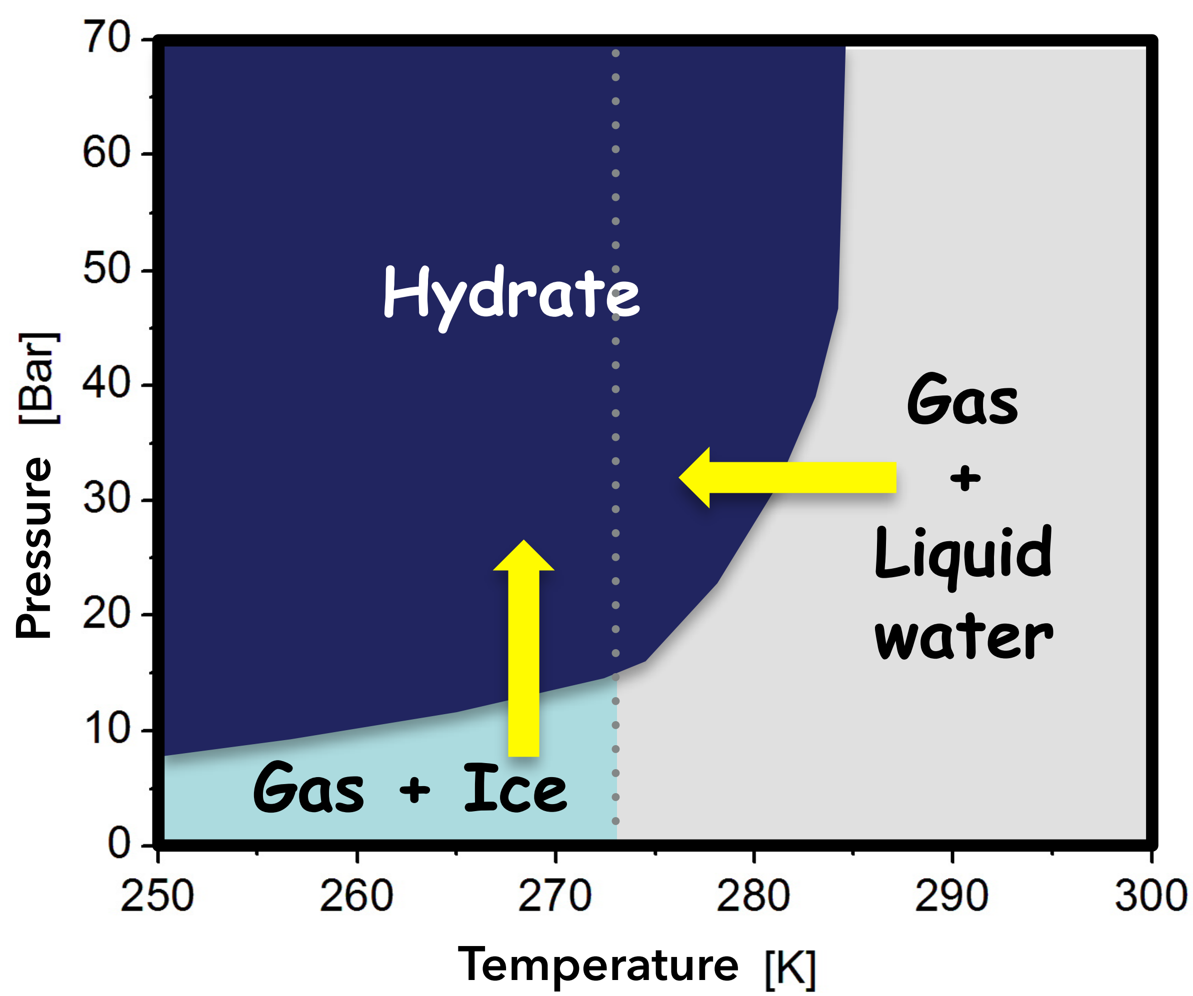


- SEMI-CLATHRATE HYDRATES:
  Super-protonic conductivity and new applications

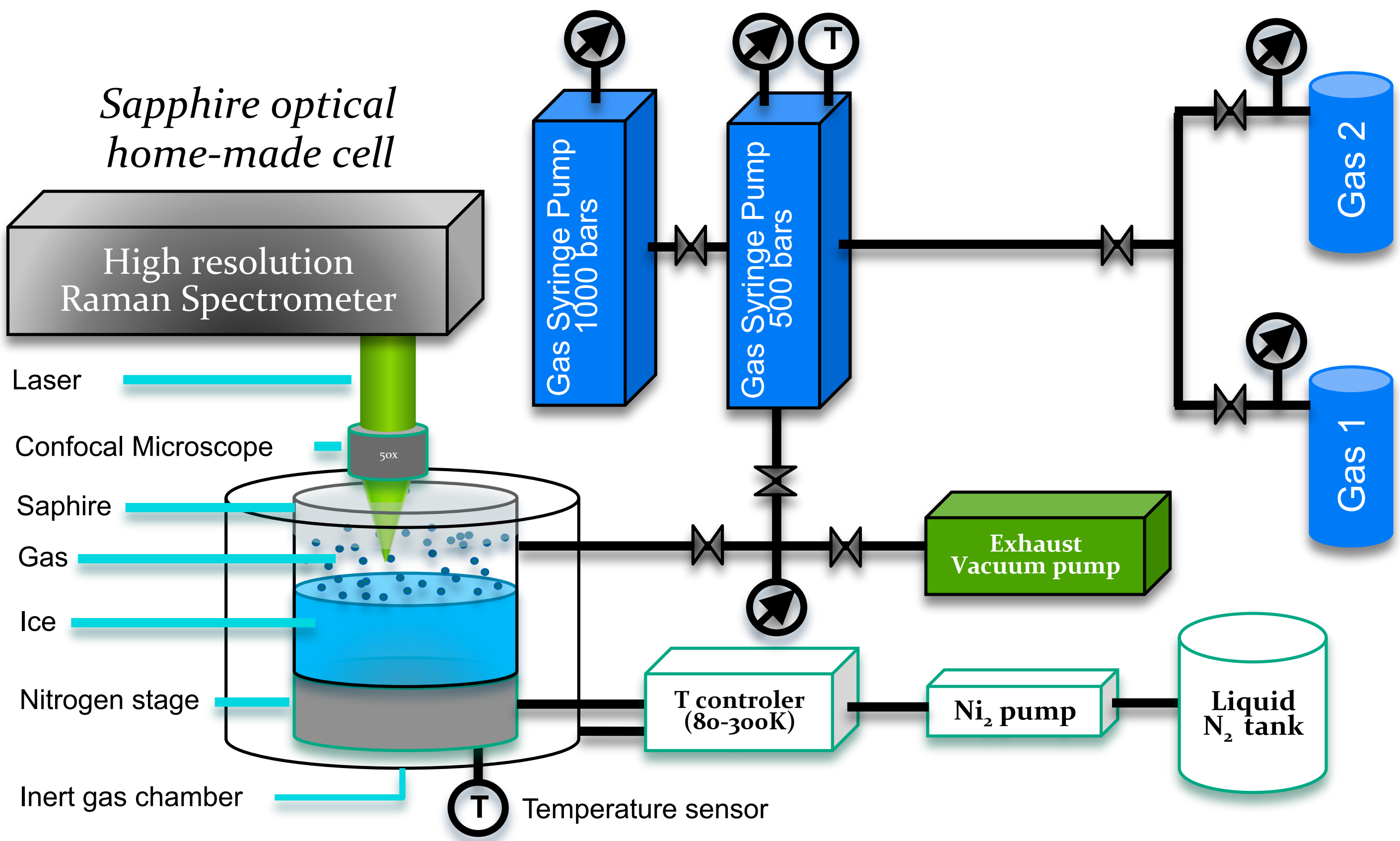
METHODOLOGY

FORMING GAS HYDRATES?

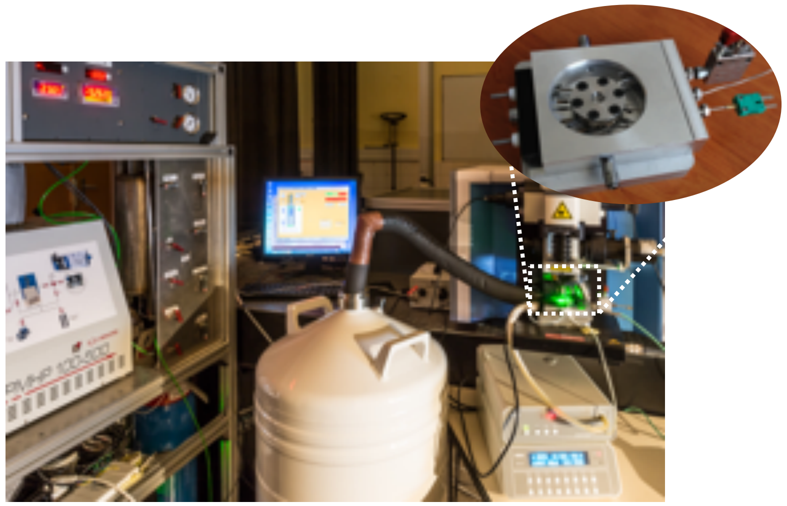
- **Pressurizing ice along isotherm** or cooling liquid water along isobar



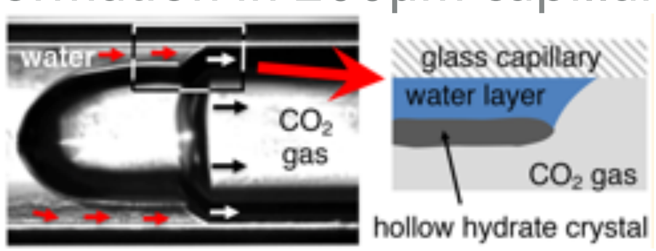
RAMAN: A MICROSCOPIC AND CHEMICALLY SENSITIVE TOOL.



Sapphire optical cell (½ cm^3)



Formation in 200µm capillary

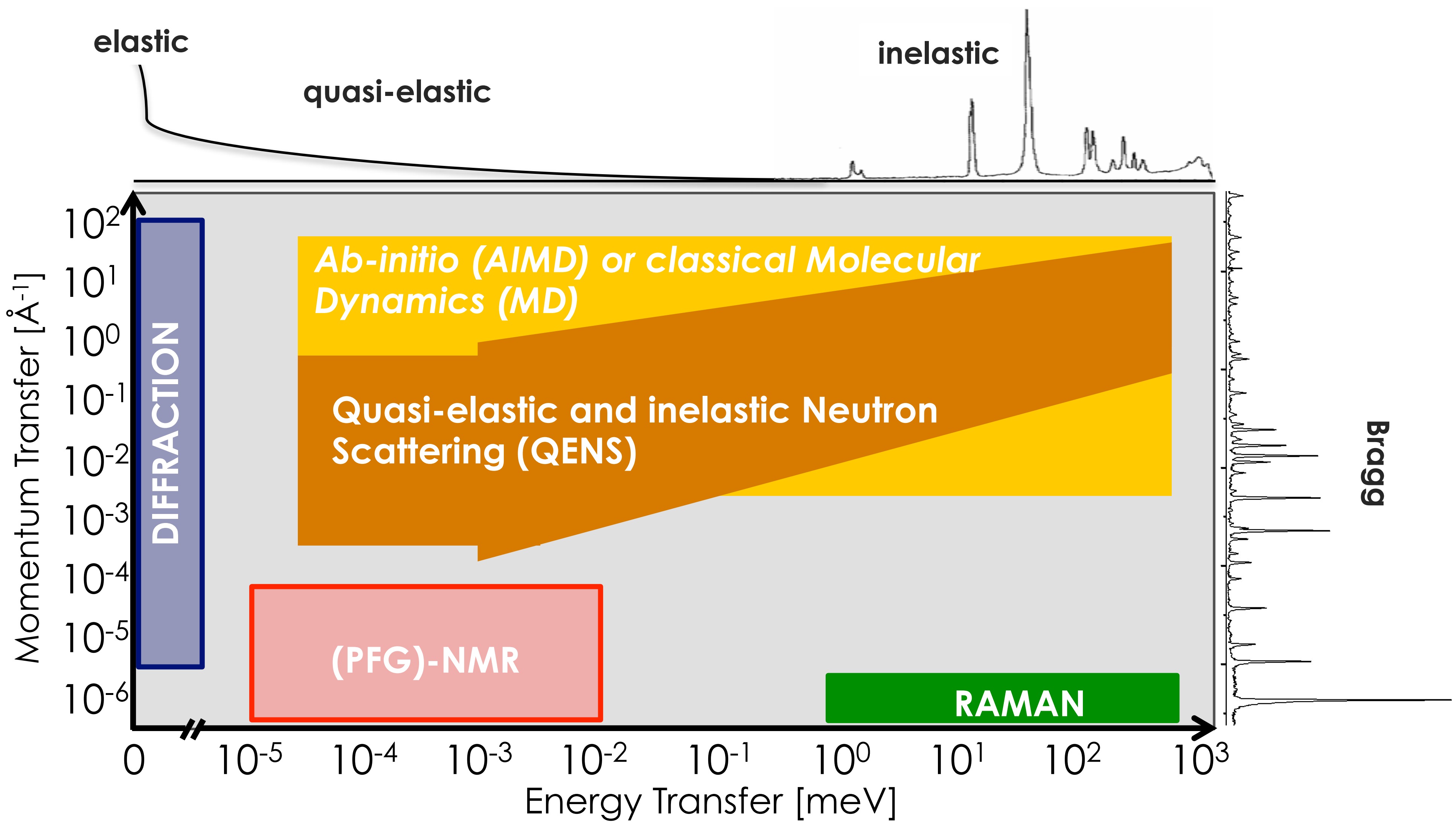


A. Touil *et al*, Langmuir. 2019

Raman spectra and imaging with µm spatial resolution

- 7 HJY confocal microspectrometers with excitation wavelengths ranging from UV-vis to InfraRed.
- Gas pressure range from 1 to 700bars
- Temperature range from 80K to 1000K
- High-pressure sample cells: autoclave (5 cm^3) // sapphire optical cell (½ cm^3) // capillary system (200µm)

METHODOLOGY

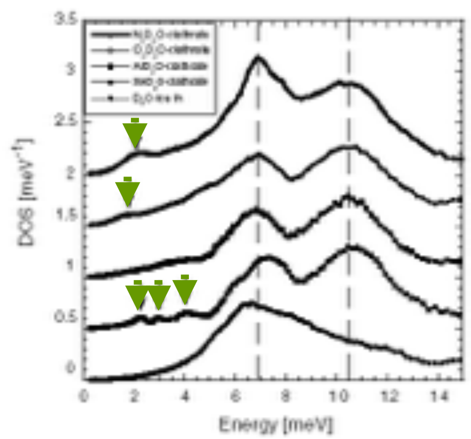


- **Molecular Dynamics / Neutron spectroscopy**: overlapping region of the reciprocal space
- **Quantum Chemistry Calculations / Neutron diffraction**: structural stability

EXAMPLES OF NEUTRON SCATTERING CONTRIBUTIONS

- **Inelastic scattering**

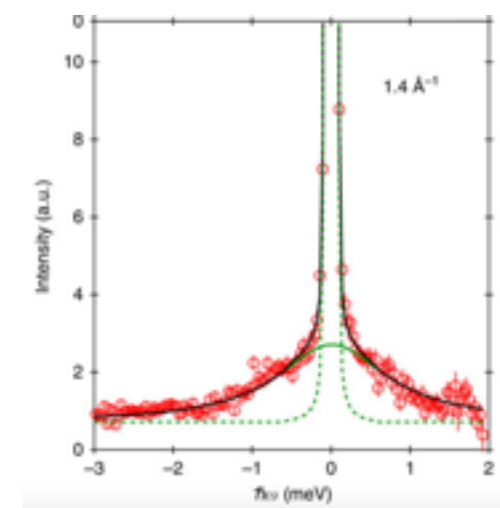
e.g. Guest rattling and phonons:
abnormal thermal conductivity



H. Schober et al Eur. Phys. J. E 12, 41 (2003)

- **Quasi-elastic neutron scattering**

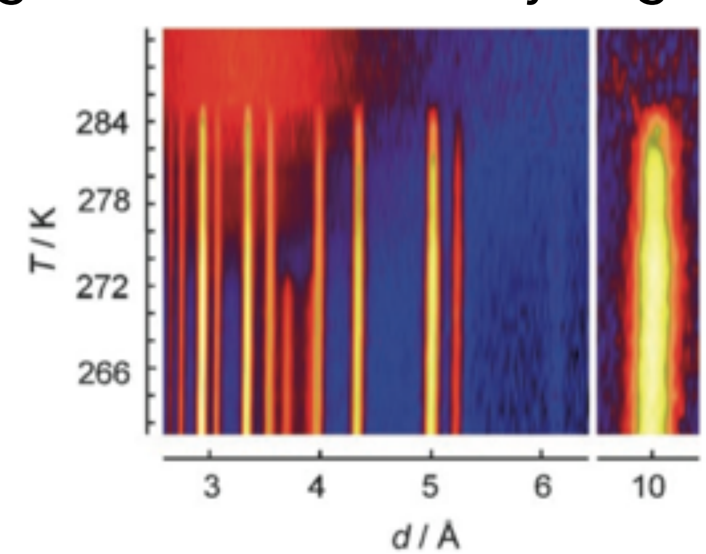
e.g. Methane hydrate:
guest boundary diffusion at GPa pressure



U. Ranieri *et al,* Nature Comm. 8, 1076 (2017)

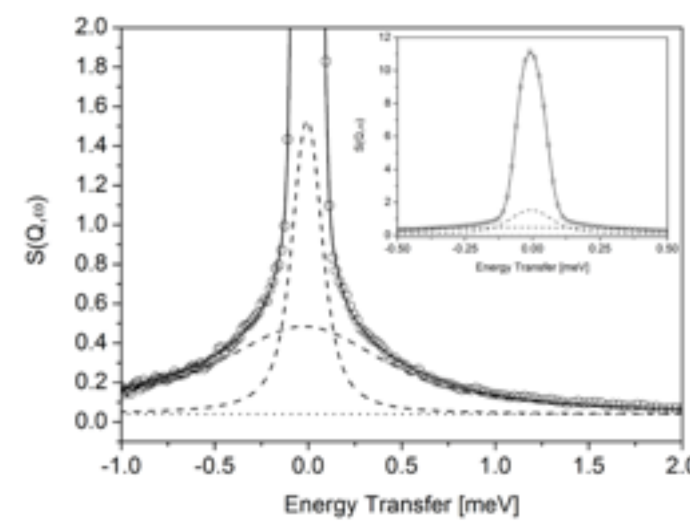
- **Diffraction**

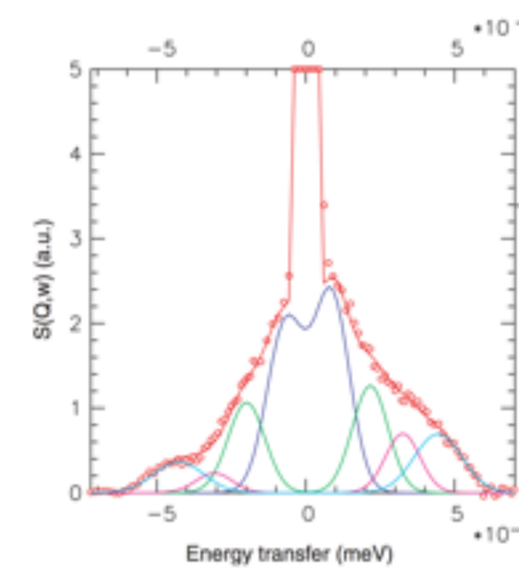
e.g. *in-situ* diffraction: hydrogen insertion



F.M. Mulder *et al*, Chem Phys Chem 9 (2008) 1331.

e.g. Gas hydrate: guest dynamics and tunneling





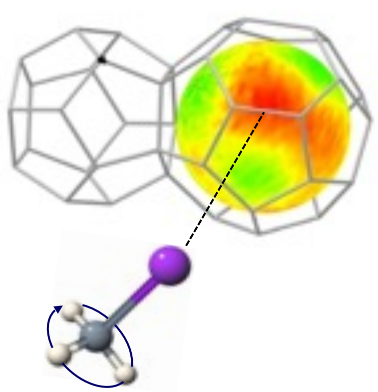
E. Pefoute *et al,* Chemical Physics 496, 24-34 (2017) M. Prager *et al,* Phase transitions 80, 473 (2007)

COMPARING QUASI-ELASTIC NEUTRON SCATTERING AND MD

- **example of the methyl iodide clathrate hydrate (melting: 277K at atmospheric pressure)**

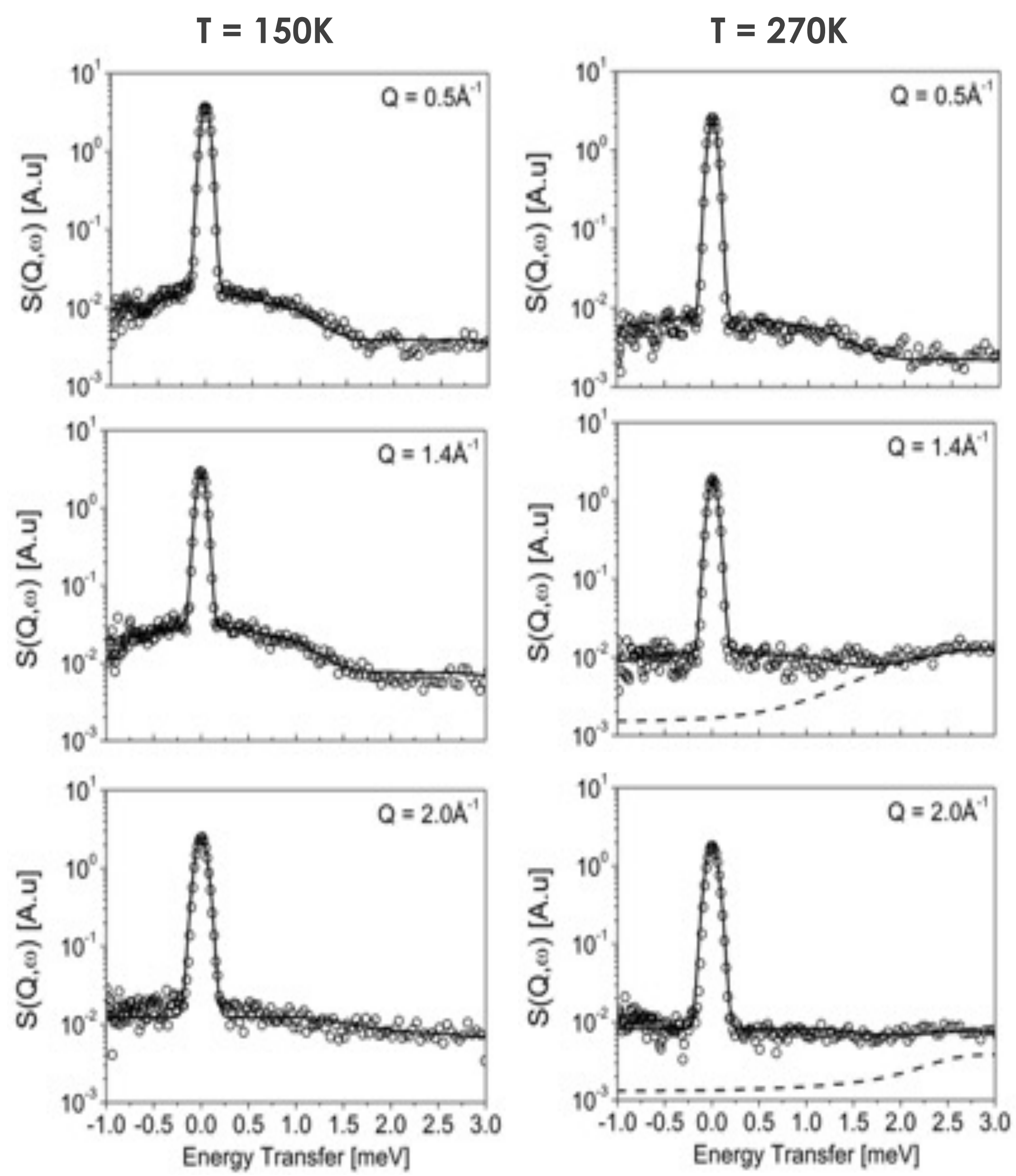
○ **QENS**

NEAT@HZB, Berlin
ΔE ≈ 100μeV
λ_0 = 5.1Å



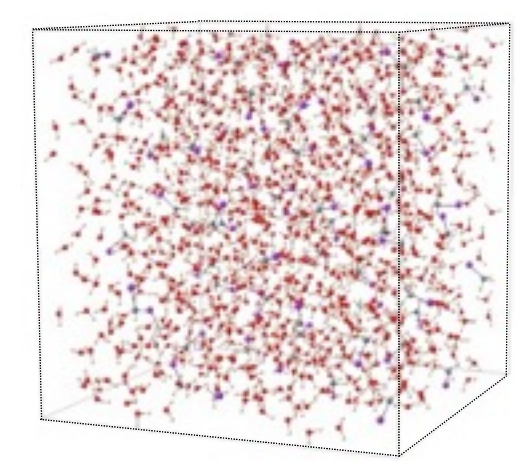
CH_3I – $17D_2O$ (type II)

Probing the cage energy landscape through the guest dynamics: existence of adsorption sites at the cage surface



—— **MD**

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



QENS: VALIDATION OF COMPLEX MD SIMULATIONS OVER A WIDE Q-T RANGE

J.Phys.Chem.C, **115(26)**, 12689 (2011)

GAS HYDRATES:
METASTABILITY, MOLECULAR SELECTIVITY
. . . TOWARDS NATURAL GAS HYDRATES

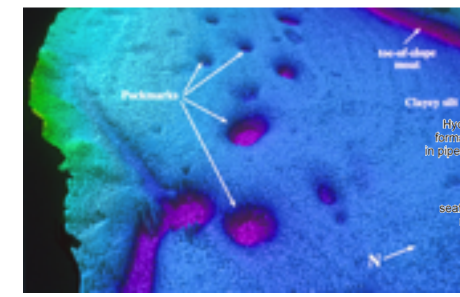
SELECTIVITY, STABILITY, CAGE OCCUPANCY, FORMATION?

Earth

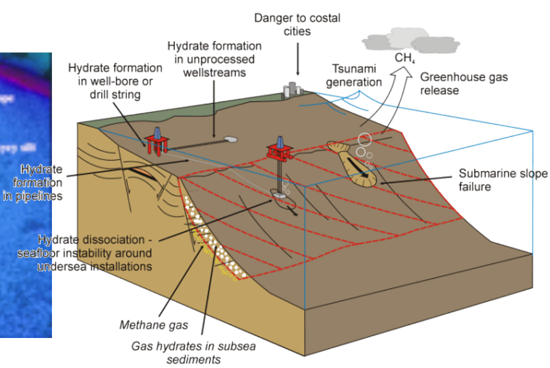
- Natural gas hydrates (NGH): existence of huge methane reservoir in deep ocean seafloor and permafrost
- 1m^3 NGH <=> 164m^3 free CH_4 gas

ENERGY RESSOURCE?

pockmarks



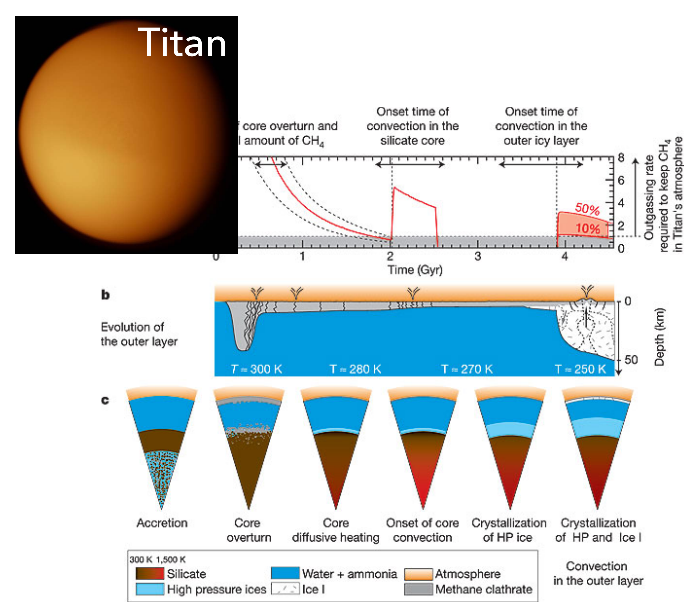
submarine avalanche



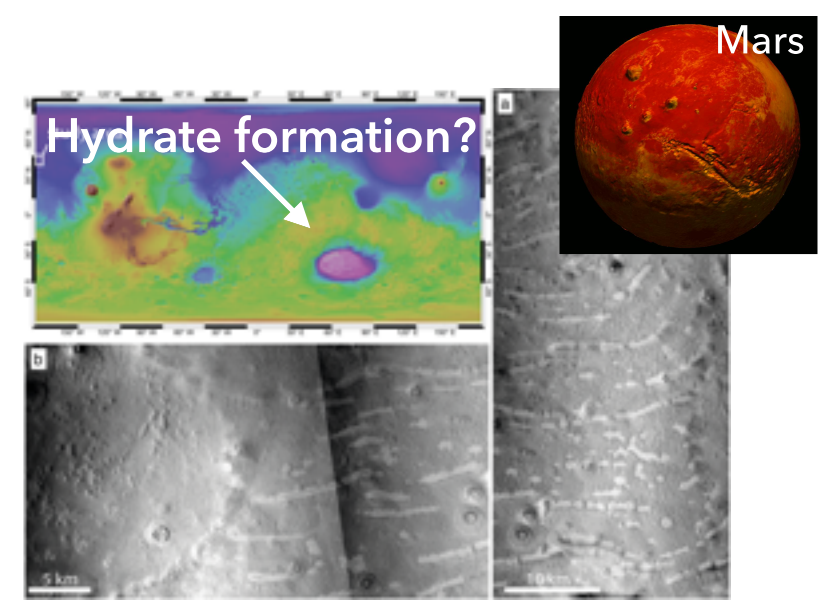
GEOHAZARDS, CLIMAT ISSUES

e.g. Titan, Mars

- Gas hydrates are supposed to occur in many planets and comets…



G. Tobie *et al*, *Nature* **440** (2006) p.61

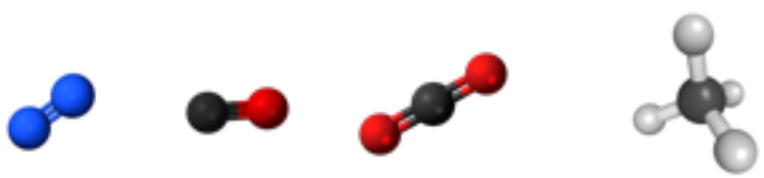


B. de Toffoly *et al*, *Scientific Report.*, **9** (2019) 8603

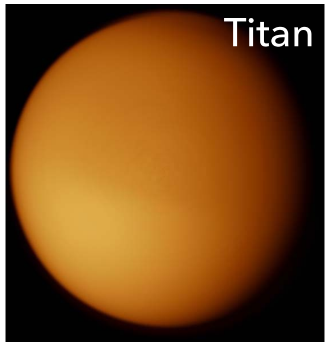
ONLY INDIRECT EXPERIMENTAL EVIDENCE AND MODELS.

MIXED GAS HYDRATES (SEVERAL GUEST SPECIES)

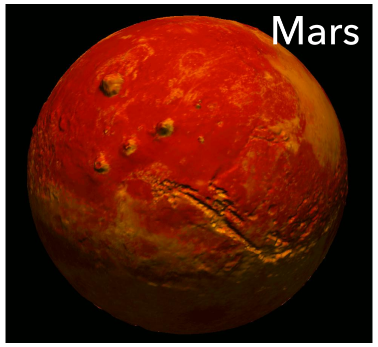
- Relevant for astro/geo physics
  - Abondant elements:



N_2 CO CO_2 CH_4 and more…

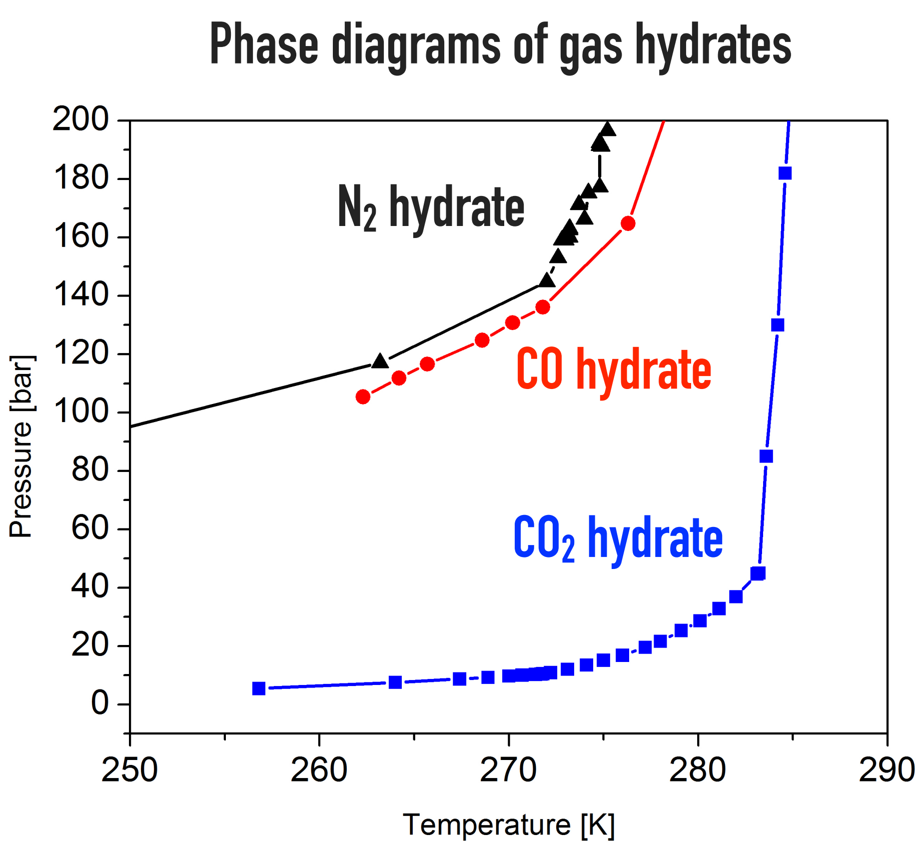


- Surface: 94K / 1.5 atm
- Atmosphère: 87-99% N_2, 1-6% CH_4 0-6% Ar



- Surface: 150-300K 0.006 atm
- Atmosphère: 95% CO_2 N_2, H_2O

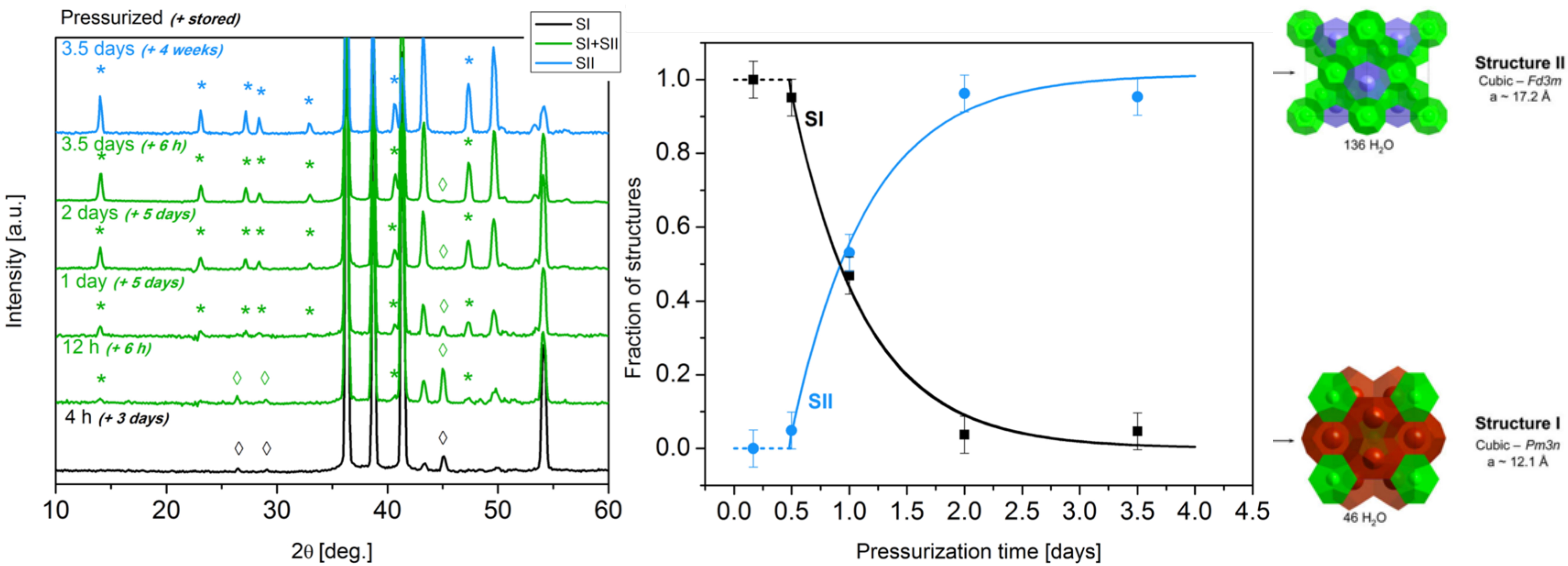
- Relevant for physical-chemistry
  - Steric hindrance
  - P-T conditions of formation
  - Water solubility
  - Dipolar moment, etc.



STRUCTURAL METASTABILITY

METASTABILITY

- Time evolution of the structure: N_2 hydrate
  - **Gas hydrate formed by pressurizing D_2O at 255K and 200 bar**
  - Powder Neutron diffraction (l_0= 2.43Å) **on** G4.1@LLB, Saclay, France at 80K / 1 bar



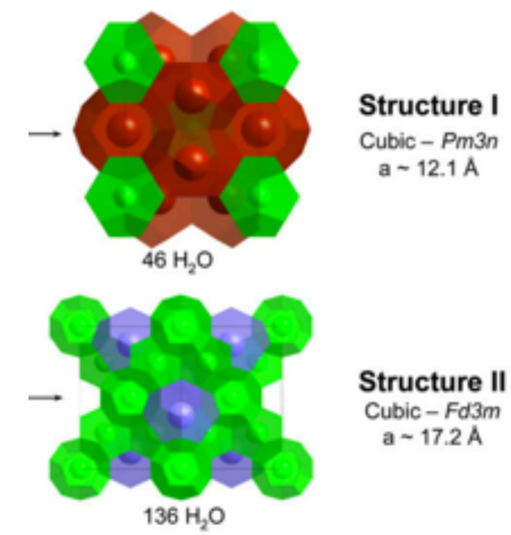
- **SI: KINETICALLY FAVORED**
- **SII: THERMODYNAMICALLY STABLE**
- **FROM SI TO SII OVER 3-4 DAYS!**

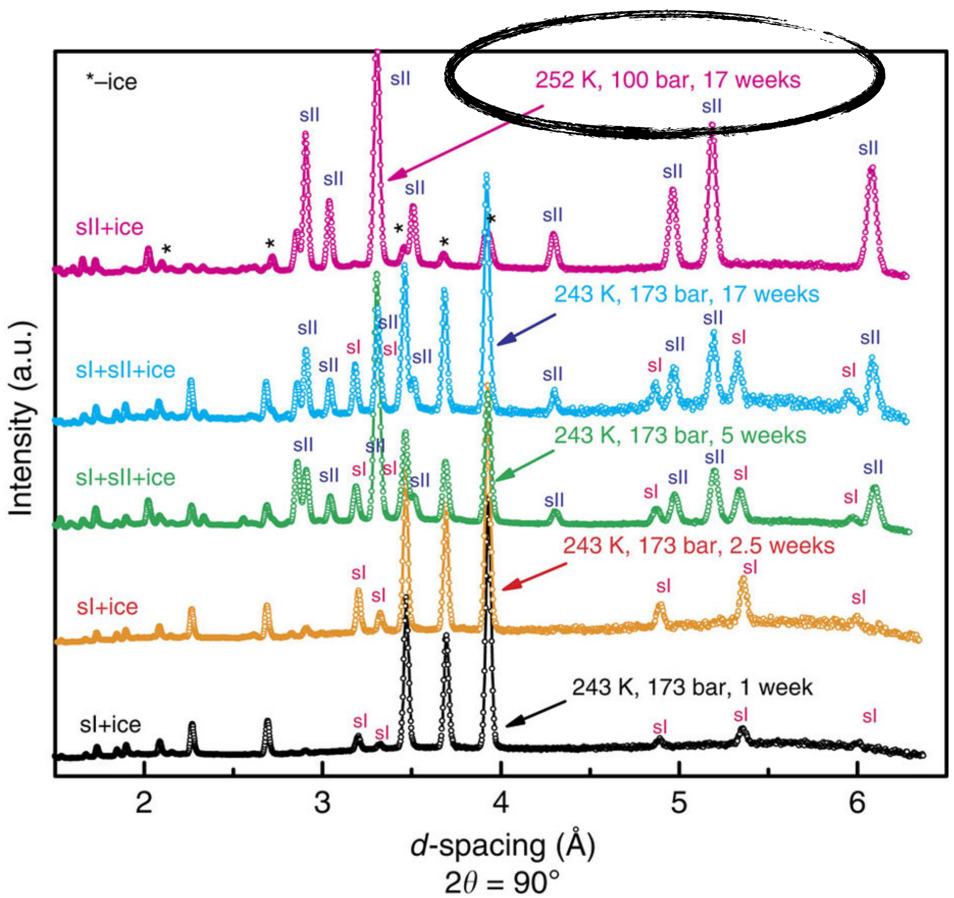
Lifetime of SI structure (induction time) = 0,5 day
Transformation rate (SI to SII) = $1{,}37 \pm 0{,}17\ 10^5\ s^{-1}$

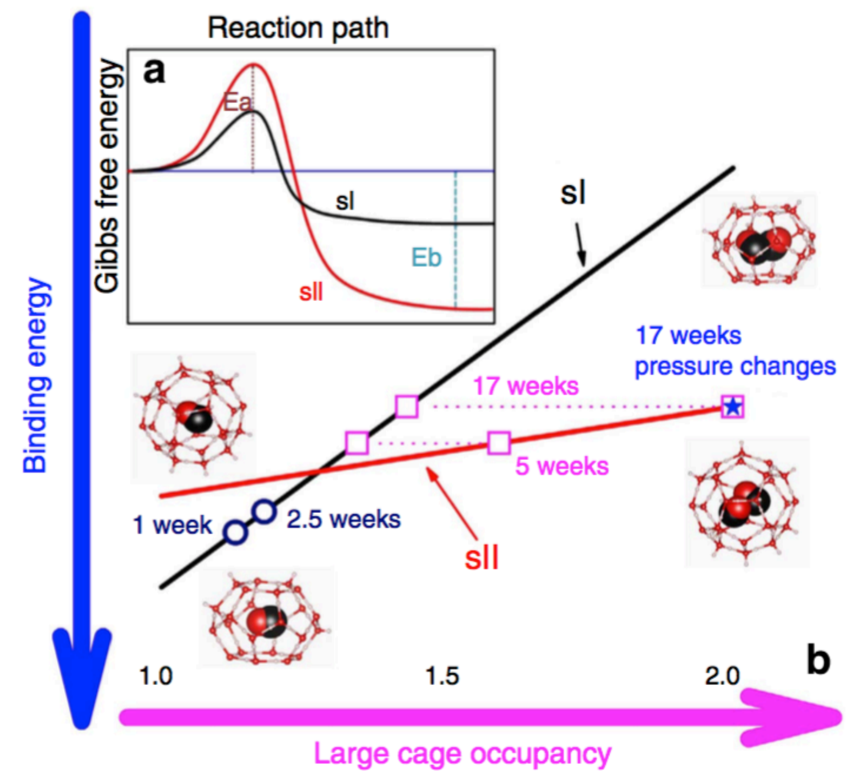
Petuya et al, J. Phys. Chem. C, 2018

METASTABILITY AND CAGE OCCUPANCY

- Time evolution of the structure: CO hydrate







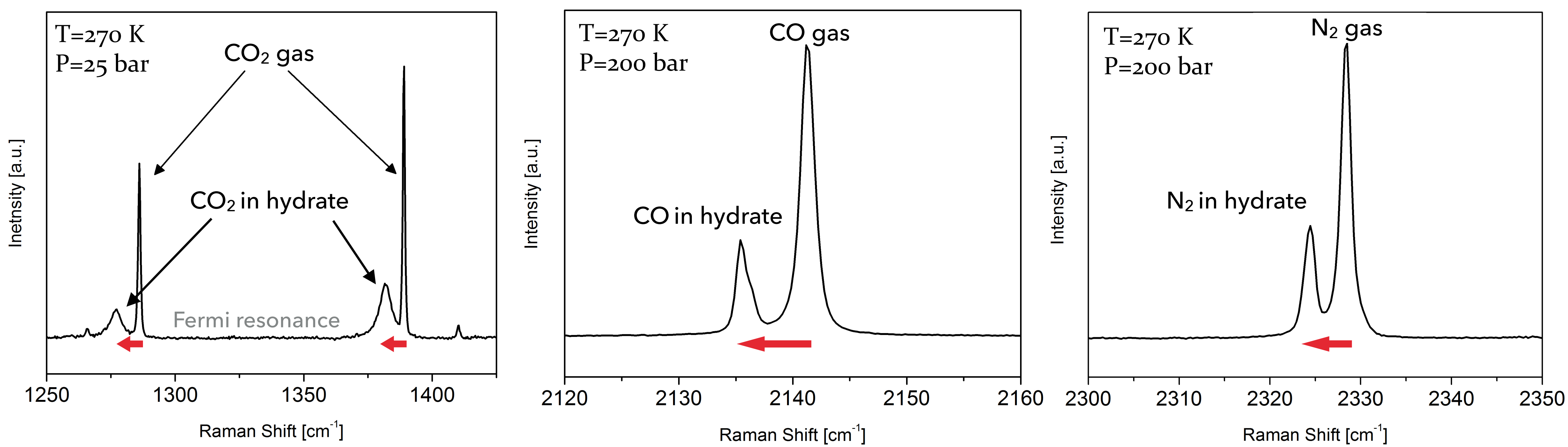
SI TO SII TRANSFORMATION OVER 17 WEEKS!

DRIVING FACTORS:
CAGE OCCUPANCY + GUEST BINDING ENERGY

Zhu et al, Nature (2014) // Petuya et al, J. Phys. Chem. C (2017)

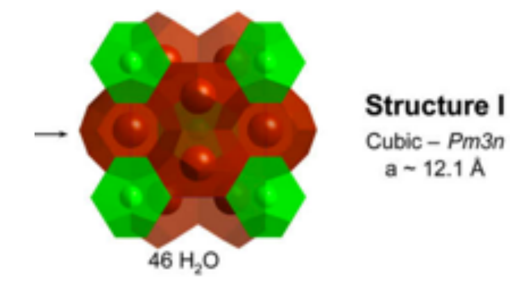
RAMAN SIGNATURES OF ENCAPSULATION

- Comparing gas and hydrate Raman signals (CO_2, N_2 and CO)



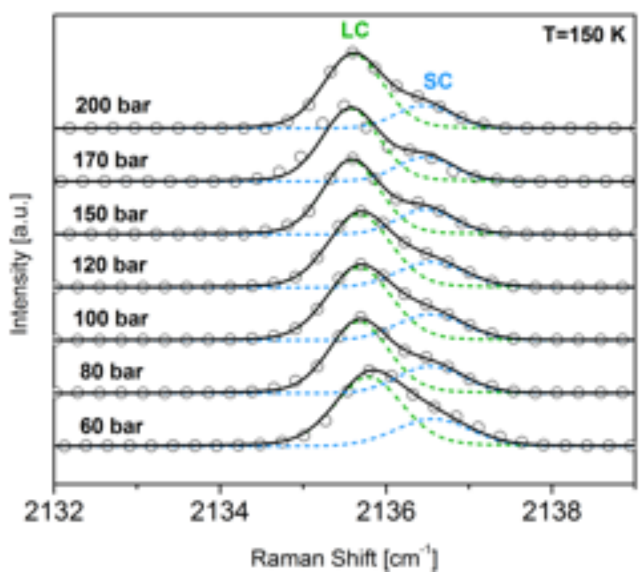
CONFINEMENT EFFECT: SHIFT TOWARDS LOWER FREQUENCIES

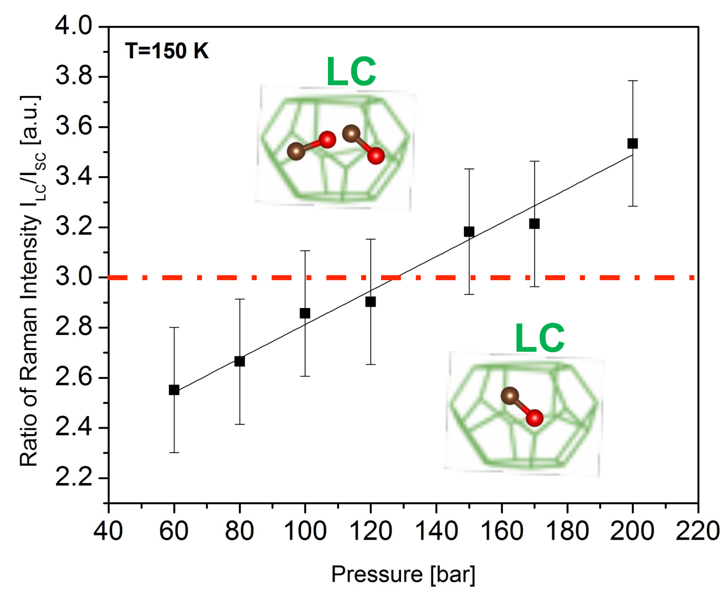
EXAMPLE OF CARBON MONOXIDE HYDRATE



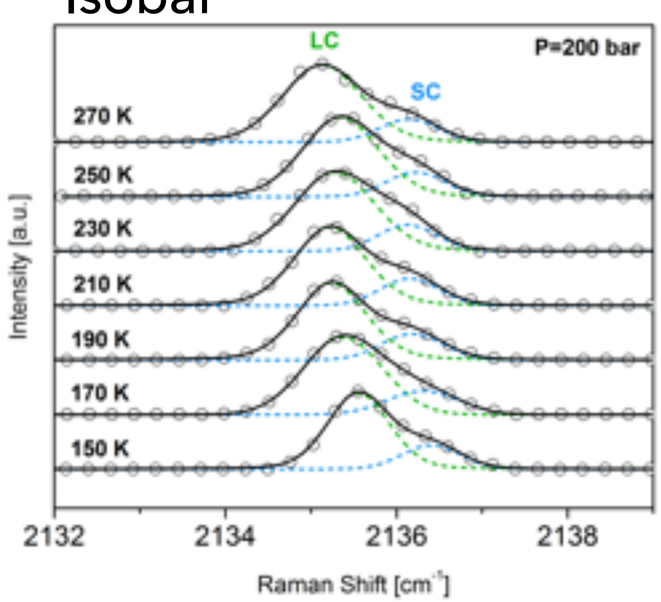
- Investigating P-T dependence in the CO hydrate by means of Raman scattering

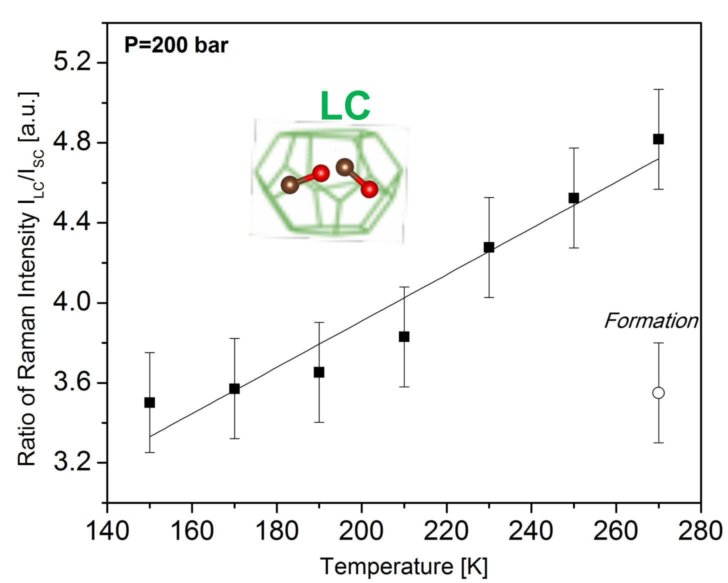
Isotherm

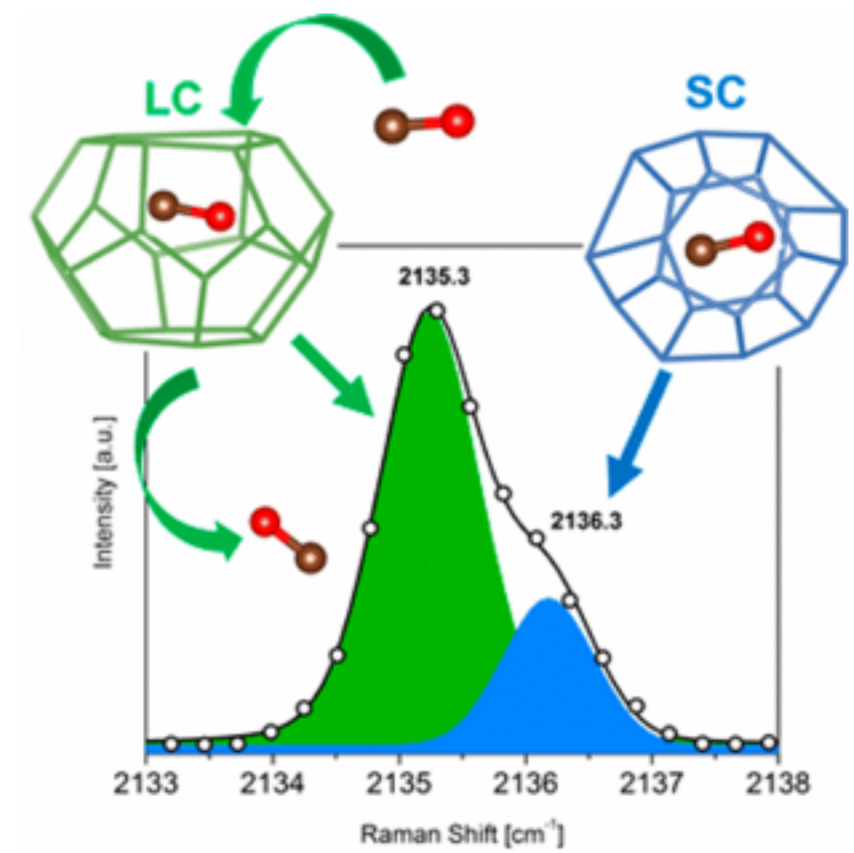




Isobar







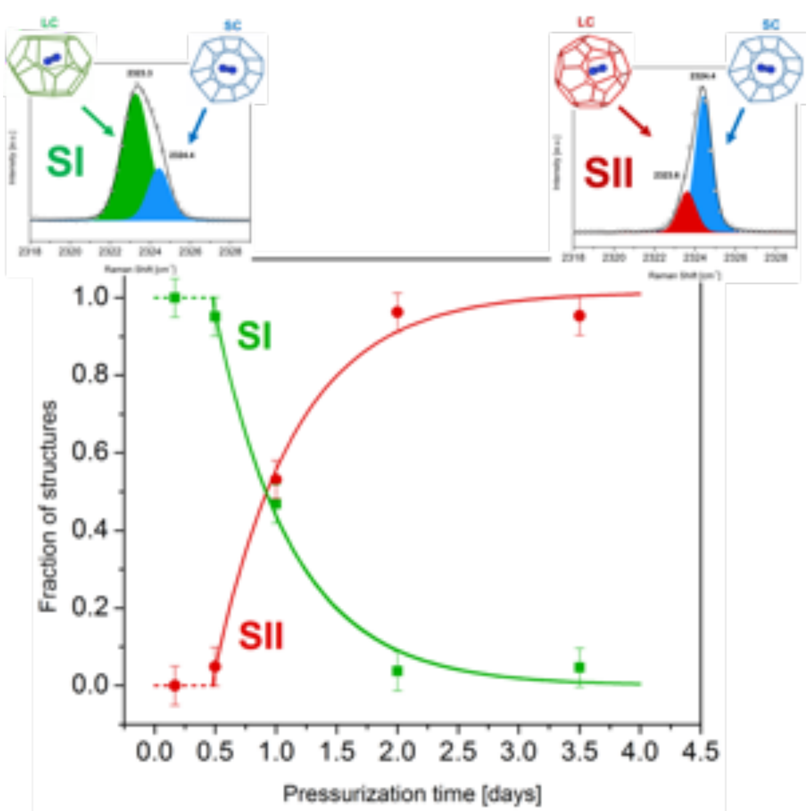
LARGE CAGE CAN EASILY CATCH AND RELEASE CARBON MONOXIDE

Petuya et al, J. Phys. Chem. C, 121(25) (2017) 13798–13802

EXAMPLE OF NITROGEN HYDRATE

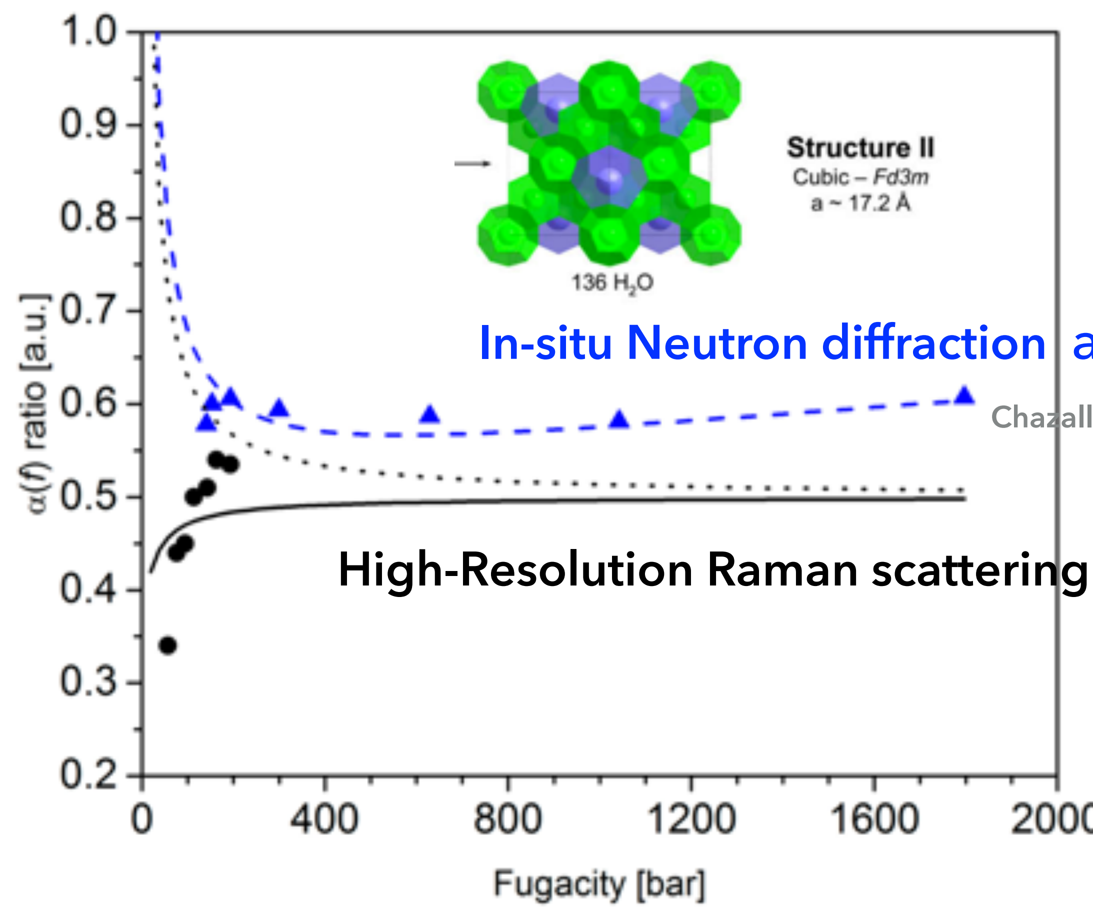
- Isotherm of guest occupancy in the N_2 hydrate and Langmuir modeling

High-Resolution Raman scattering and Neutron diffraction at 80K/1bar



Petuya et al, J. Phys. Chem. C, 2018

$$\alpha(f) = \frac{\theta_{LC}(f)}{2\theta_{SC}(f)} \text{ with } \theta_{SC}(f) = \frac{C_S f}{(1 + C_S f)} \text{ and } \theta_{LC}(f) = \frac{C_{L1} f(1 + 2C_{L2} f)}{(1 + C_{L1} f + C_{L1} C_{L2} f^2)}$$



In-situ Neutron diffraction at 273K : $C_S < C_{L1}$

Chazallon et al, J. Chem. Phys. (2002)

High-Resolution Raman scattering at 150K : $C_S > C_{L1}$

Petuya et al, Crystals (2018)

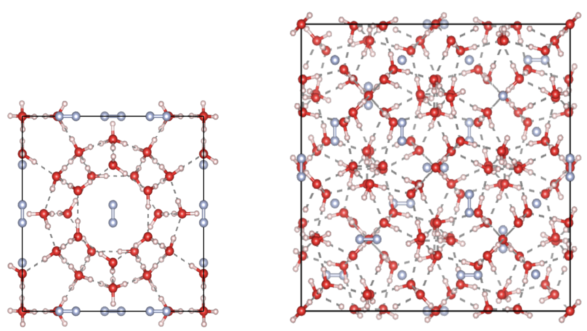
AT 150K: INVERSION OF THE LANGMUIR CONSTANTS IN LARGE CAGE AND IN SMALL CAGE

Petuya et al, J. Phys. Chem. C (2018) // Crystals (2018)

QUANTUM CHEMISTRY MODELLING

- N_2 hydrate: Density Functional Theory (DFT) calculations of the hydrate stability

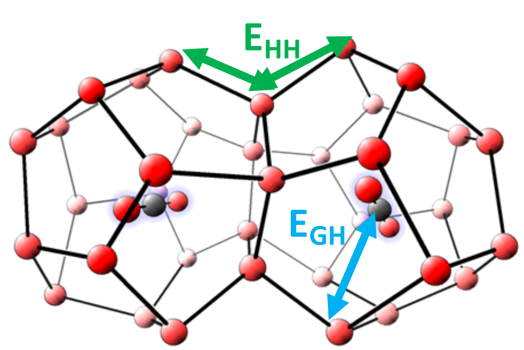
  - Computing the potential energy of complete unit cells with various large cage occupancy

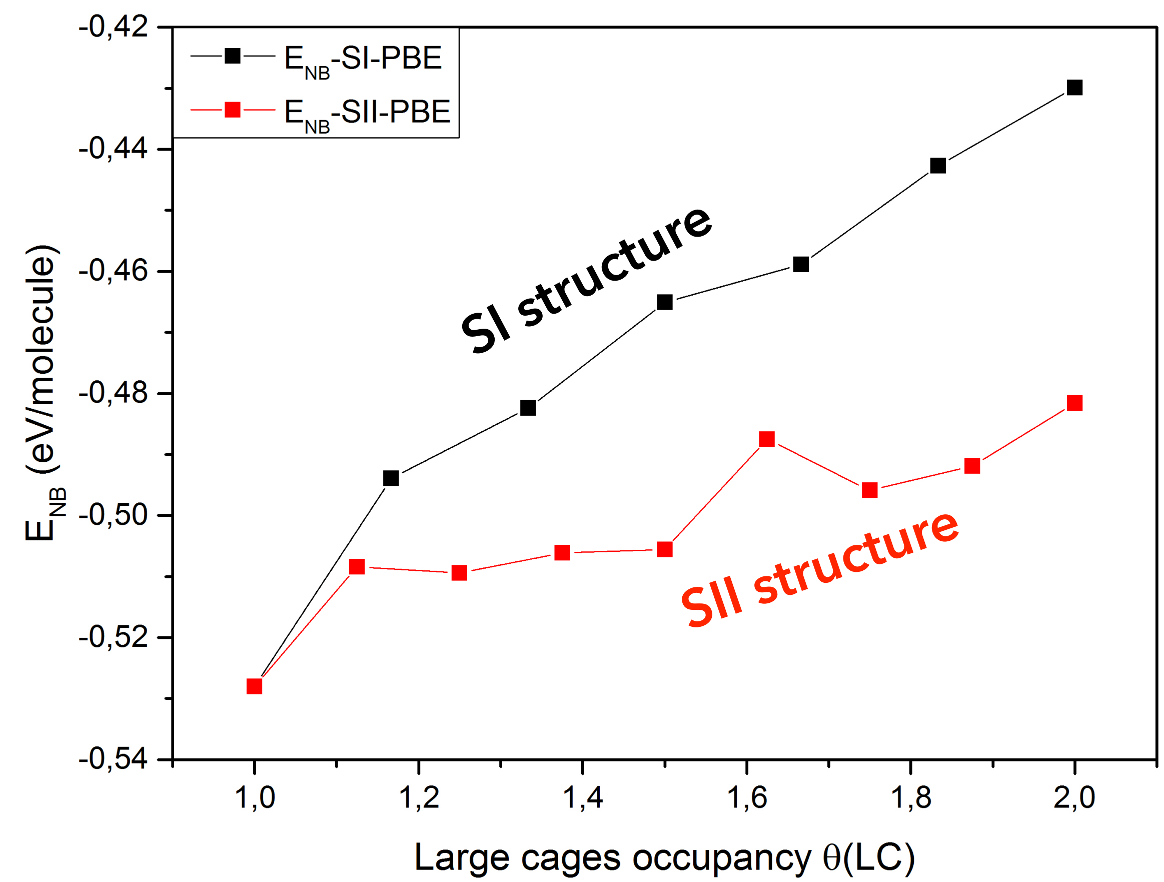


SI (12Å) SII (17Å)

  - Extracting the non-bonding energy E_{NB} :

$$E_{NB} = E_{GG} + E_{GH} + E_{HH}$$





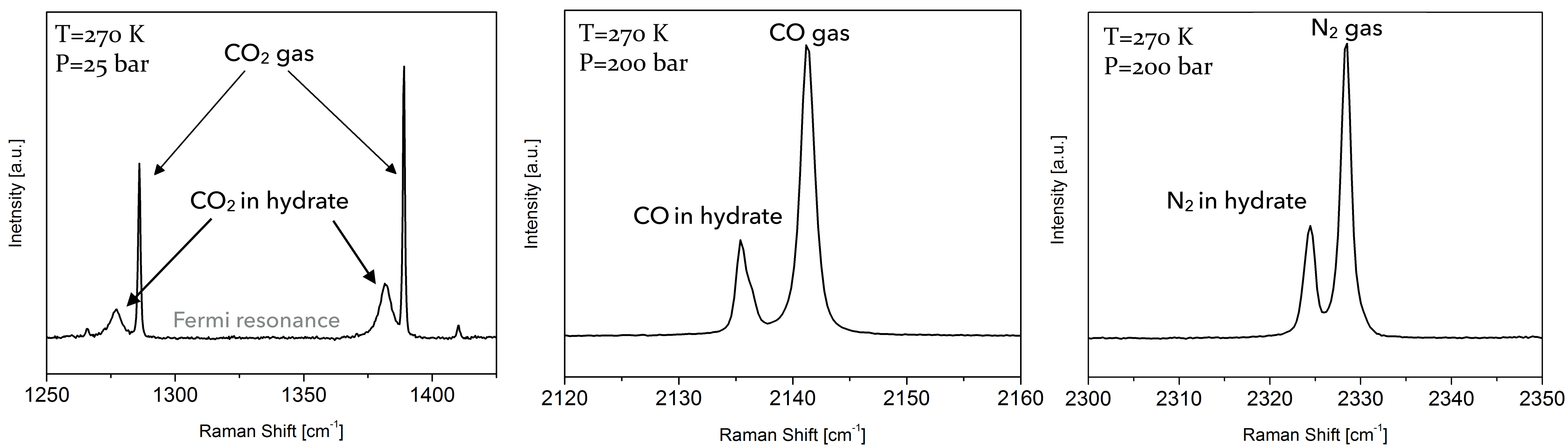
DOUBLE OCCUPANCY OF THE LARGE CAGE
➜ SI MORE DESTABILIZED THAN SII

Metais et al, to be submitted (2020)

SELECTIVITY

SELECTIVITY BY MEANS OF RAMAN SCATTERING

- Comparing gas and hydrate Raman signals (CO, N_2 and CO_2)



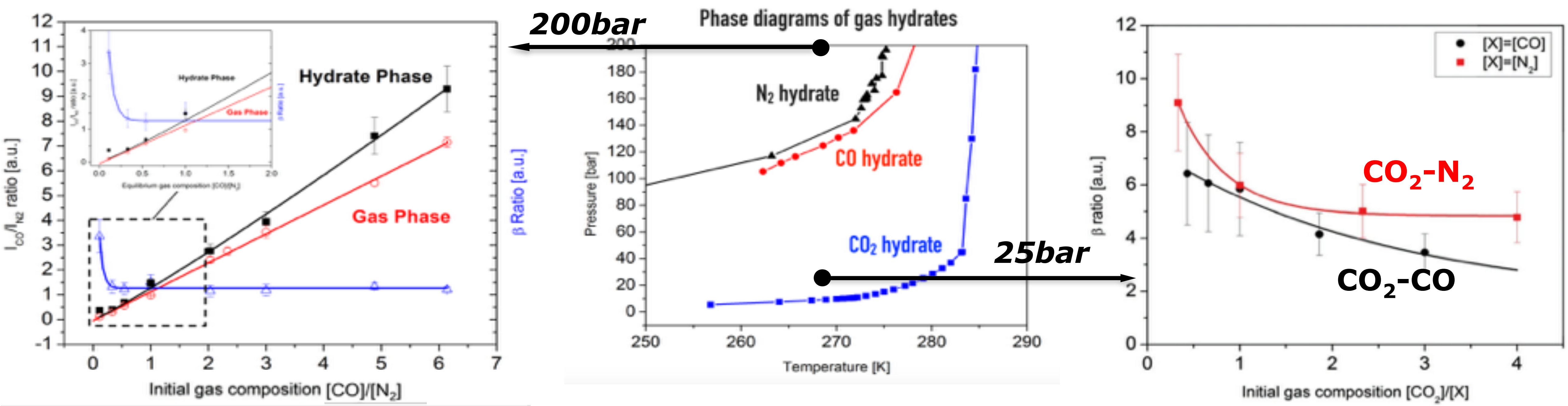
COMPARING INTENSITY RATIO IN GAS PHASE AND IN HYDRATE PHASE: ACCESSING SELECTIVE GAS TRAPPING

SELECTIVE GAS TRAPPING

- Using integrated Raman signals to measure the molecular selectivity

*Mixed **CO-N_2 hydrate***
at 270K and 200bar

*Mixed **CO_2-N_2 and CO_2-CO hydrates***
at 270K and 25bar

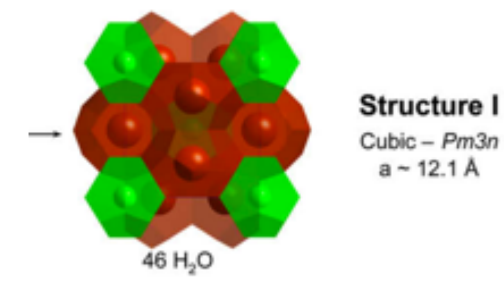


PREFERENTIAL ENCAPSULATION OF CO_2: INFLUENCE OF THERMODYNAMICS CONDITIONS

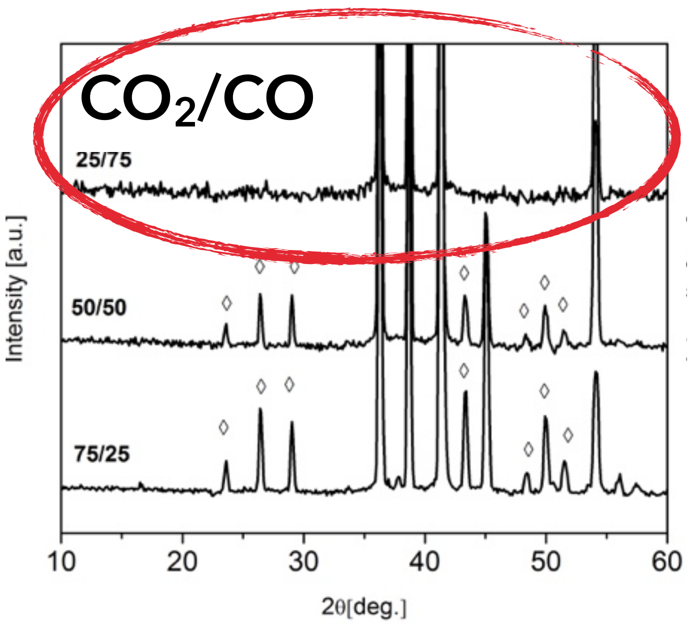
PREFERENTIAL ENCAPSULATION OF CO: INFLUENCE OF DIPOLE MOMENT

Petuya et al, Chem. Comm, 54 (2018) // J. Chem. Phys. C, 123 (2019)

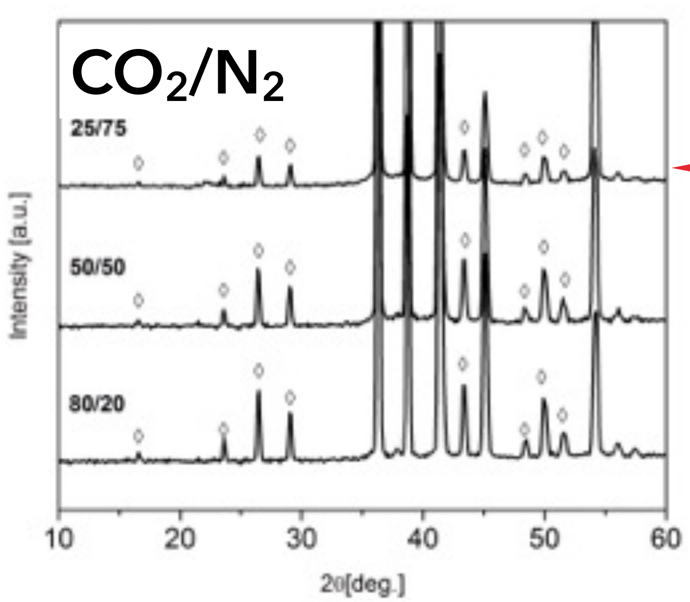
IMPEDING EFFECT OF CARBON MONOXIDE



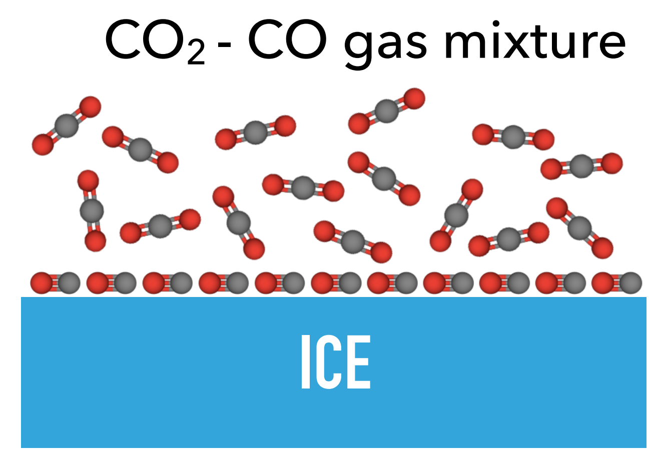
- Formation of mixed hydrates for identical PT conditions (T = 270K , P = 25 bar) and for low CO_2 concentration.
- **Powder Neutron diffraction** (l_0= 2.43Å) **on G4.1@LLB, Saclay, France at 80K / 1 bar**



No formation of mixed hydrate



Formation of mixed hydrate



- CO : better adsorption on ice than N_2 (BET coefficient)? impeding the hydrate formation mechanism?
- CO_2/CO mixed hydrate from liquid water at 25 bar and for gas mixture 10/90: successful formation.

CARBON MONOXIDE: THE SMALLEST INHIBITOR OF HYDRATE FORMATION FROM ICE!

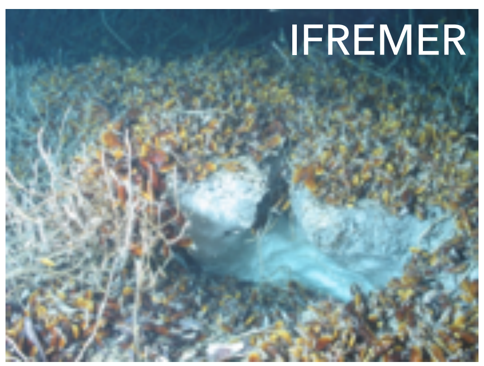
Petuya et al, Chem. Comm, 54, 2018

TOWARDS NATURAL GAS HYDRATES

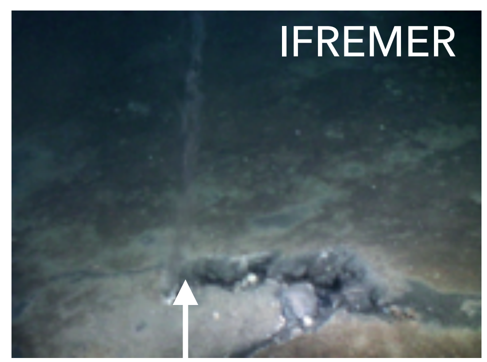
http://mi2c.hydrate.eu

TOWARDS SYSTEMS IN NATURAL ENVIRONMENTS

- Natural gas hydrate:
  Low T + High P + salt + water + gas **+ sediments (sands, clays, etc.)**



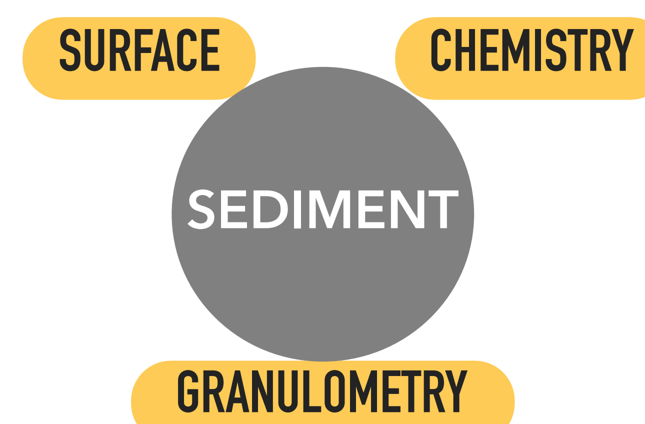
- e.g. methane hydrate
  Black sea



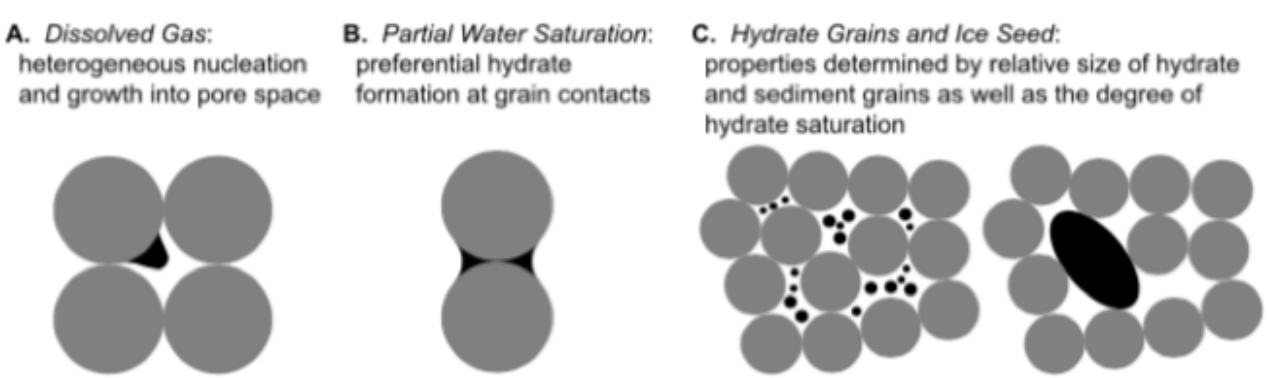
- e.g. CO_2 bubbles
  Marmara sea

IMPACT OF SEDIMENT ONTO GAS HYDRATE FORMATION (KINETICS, STABILITY, SELECTIVITY, ETC.)?

- Few sediment factors involved in the hydrate formation



- Links with seafloor stability



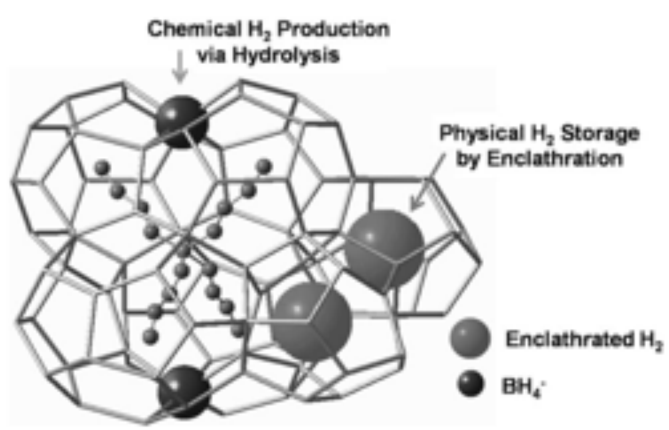
Waite, W. F., *et al.*, *Physical properties of hydrate-bearing sediments*, Rev. Geophys., 47, **2009**

SEMI-CLATHRATE HYDRATES

SEMI-CLATHRATE: HYDRATE CAGE NOT ONLY MADE OF WATER

- cages constituted of water molecules + additional species

Gas storage and separation



e.g. quaternary ammonium hydrates

gas species as co-host and/or co-guest inclusion

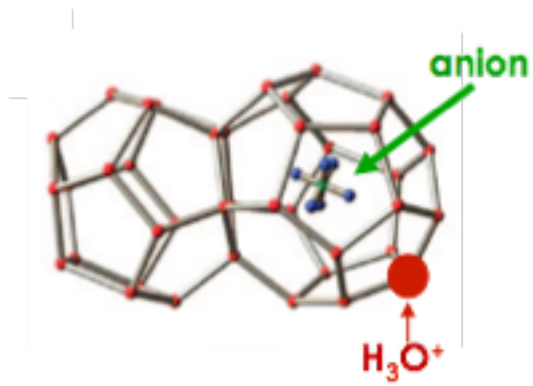
Shin *et al*, *Chem Asian J* 2010, 5, 22-34

Shin *et al*, J. Phys. Chem. A 2009, 113, 6415 – 6418.

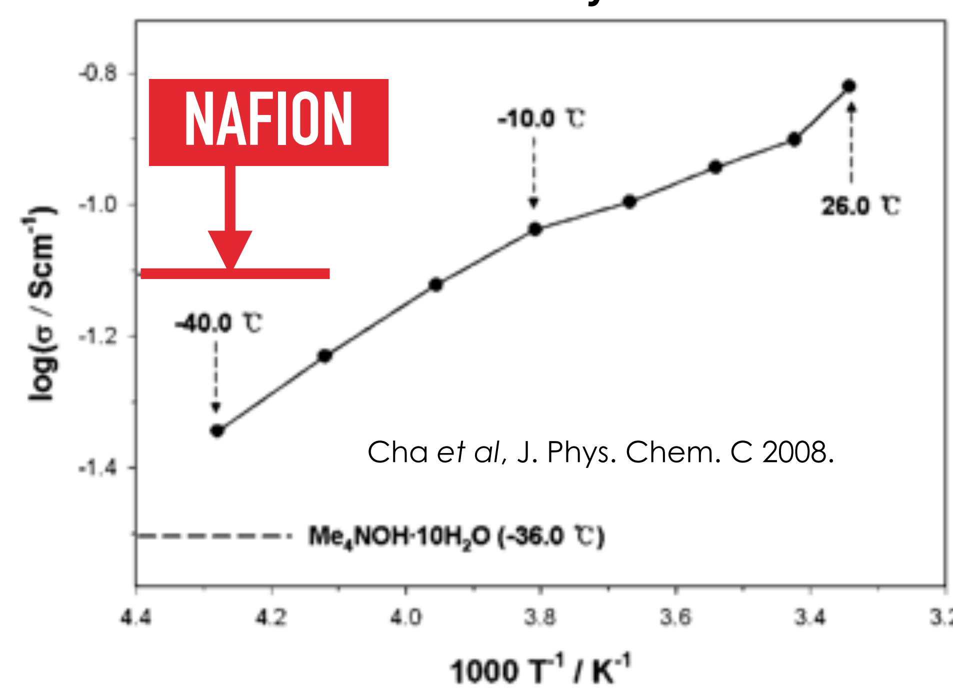
Strong acid hydrates

e.g. hexafluorophosphoric acid HPF_6 hydrate

Mootz *et al*, J. Am. Chem. Soc. 1987, 109, 1200.



Conductivity



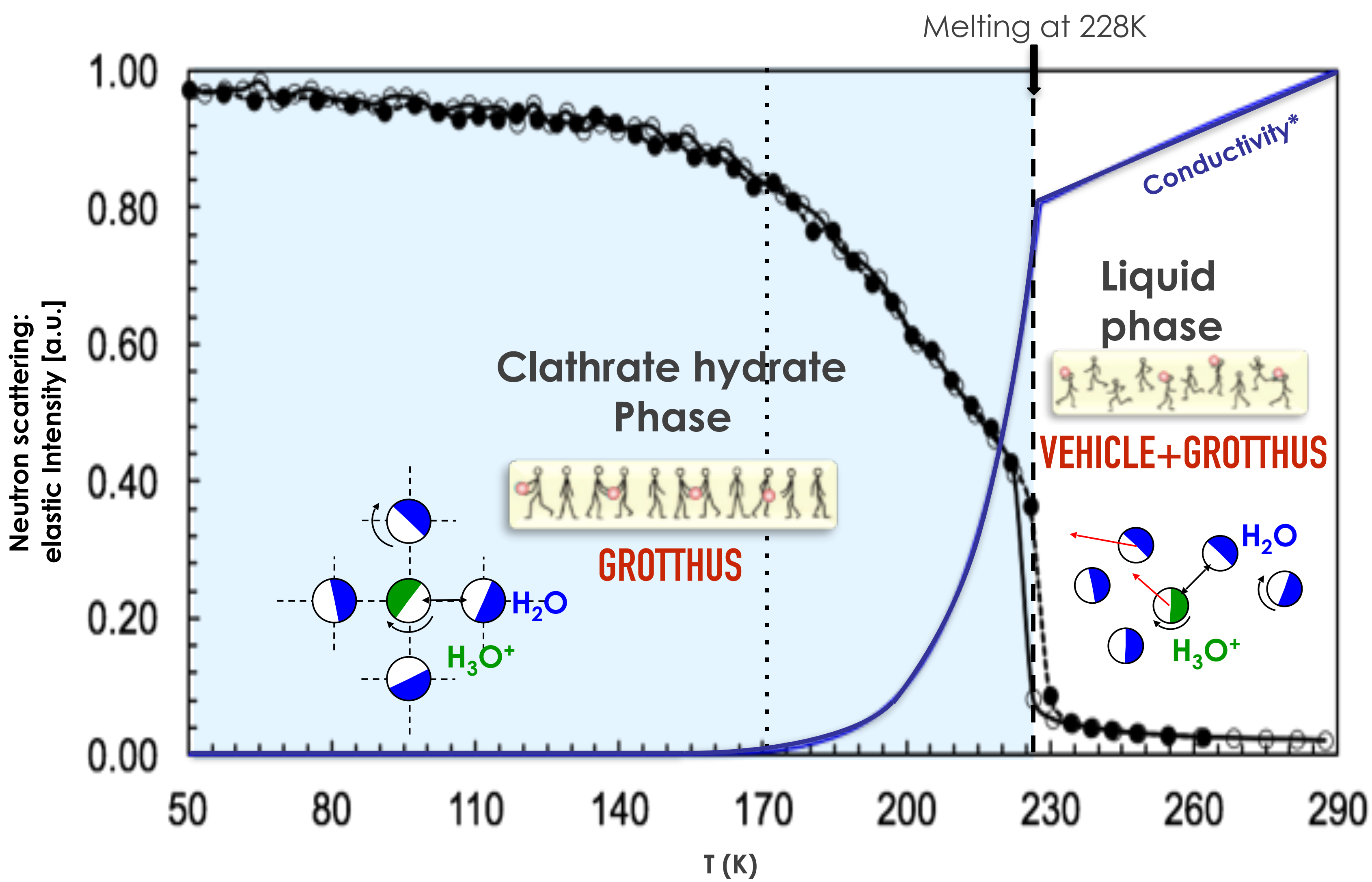
- SUPER-PROTONIC CONDUCTIVITY: MECHANISM?
- APPLICATIONS: HYDROGEN STORAGE AND A NEW FUEL CELL

PROTON CONDUCTIVITY AND HYDRATION NUMBER

PROTON CONDUCTIVITY AND MOBILITY

- Conductivity measurement and neutron spectroscopy (QENS) of the perchloric acid clathrate hydrate $HClO_4$ – 5.5H_2O (type SI)

  - Elastic Fixed Window Scan on IN10@ILL, Grenoble, France

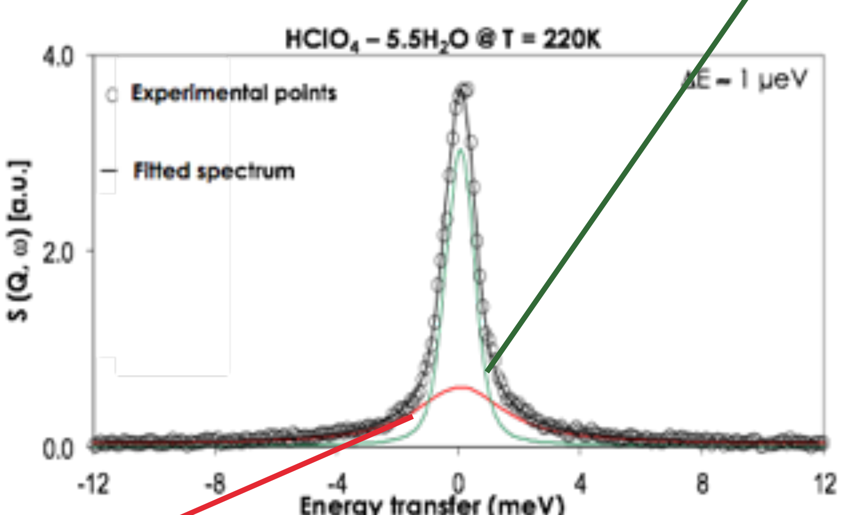


A. Desmedt *et al,* J. Chem. Phys. 121(23) (2004) 11916–11926 // // * T.-H. Huang et al, J. Phys. Chem. 92 (1988) 6874

PROTON CONDUCTIVITY MECHANISM

- Combining ^{1}H PFG NMR and Neutron Spectroscopy (QENS) to study the perchloric acid clathrate hydrate $HClO_4$ – $5.5H_2O$ (type SI)
  - QENS experiments on IN10@ILL Grenoble + NEAT@HZB Berlin

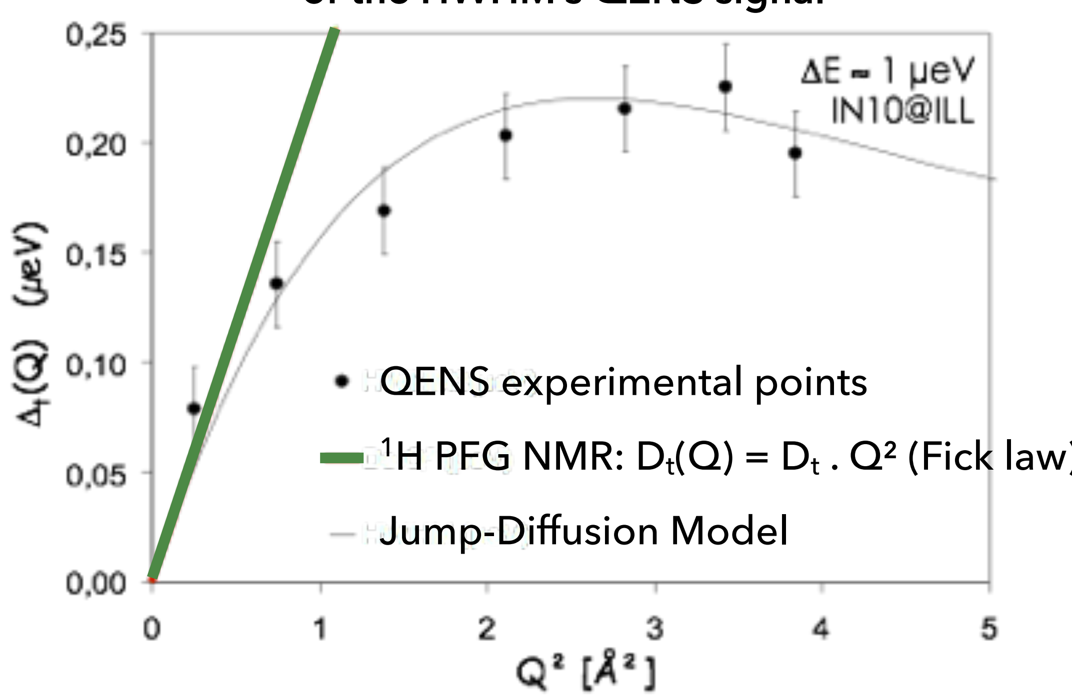
Long-range proton diffusion

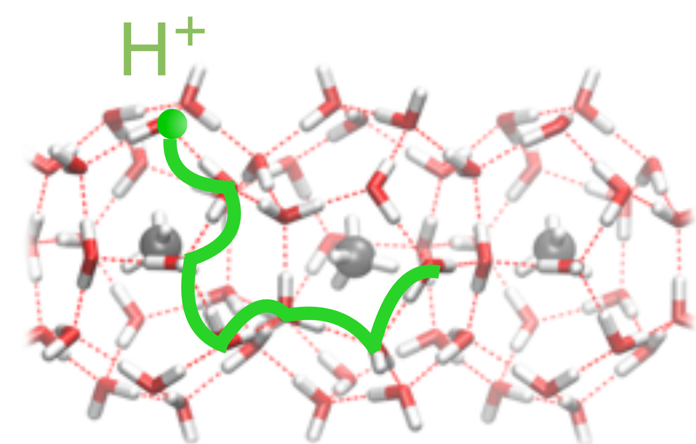


Elementary steps: water reorientations, hydronium reorientations and H-bond proton transfer

QENS by using energy resolution from 1µeV to 1 meV

Momentum transfer dependence of the HWHM's QENS signal





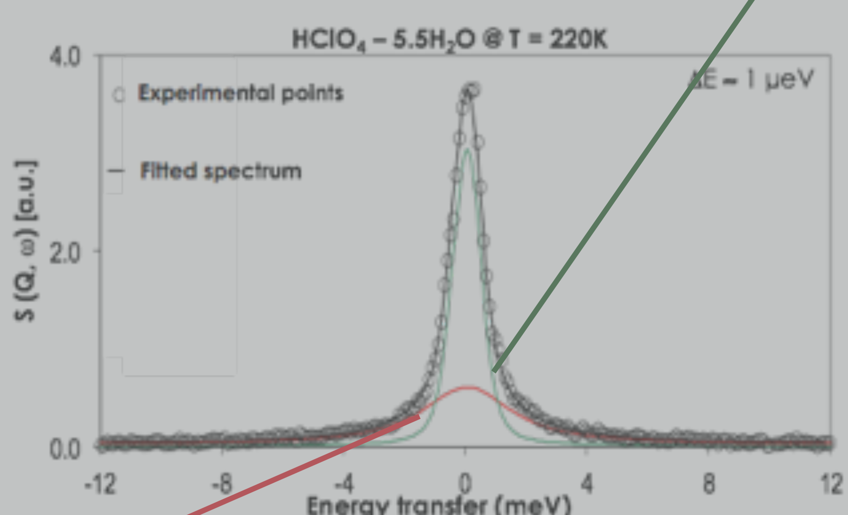
Proton hoping between water molecules of the cages with D = 3.5 10^{-8} cm^2/s @220K.

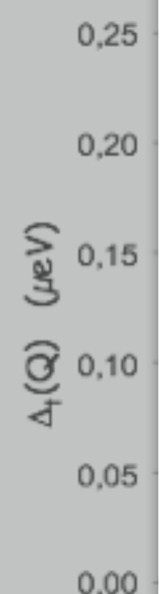
A. Desmedt *et al*, J. Chem. Phys. 121(23) (2004) 11916–11926 // Solid State Ionics, 252 (2013) 19-25

PROTON CONDUCTIVITY I

- Combining ^{1}H PFG NMR
  the perchloric acid clathr
  - QENS experi

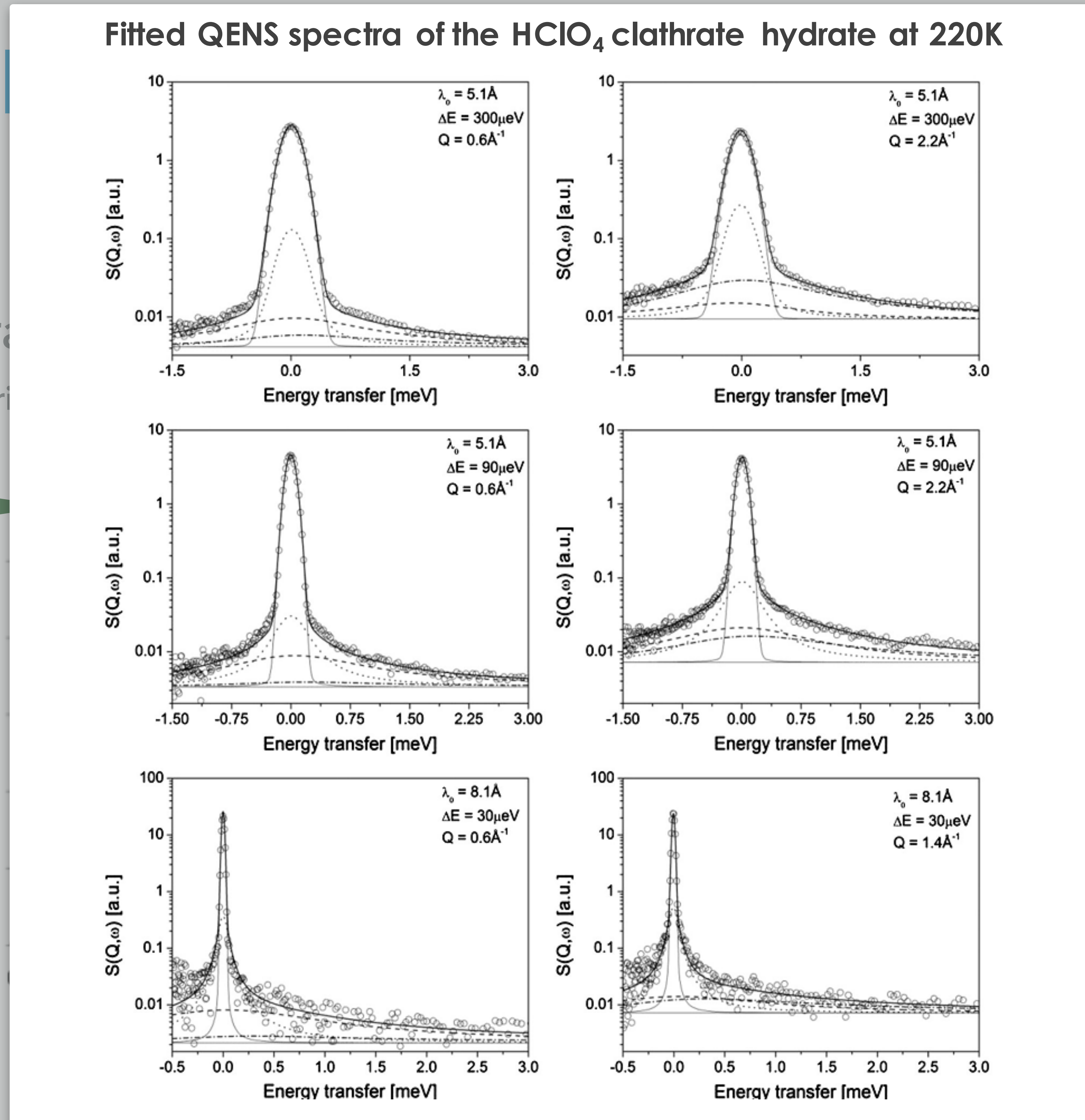
Long-range proton diffusion





Elementary steps: water reorientations, hydronium reorientations and H-bond proton transfer

QENS by using energy resolution from 1μeV to 1 meV



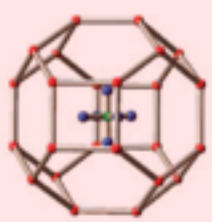
with $D = 3.5\ 10^{-6}$ cm^2/s @220K.

A. Desmedt *et al,* J. Chem. Phys. 121(23) (2004) 11916–11926 // Solid State Ionics, 252 (2013) 19-25

LONG-RANGE PROTON DIFFUSION AND CONDUCTIVITY

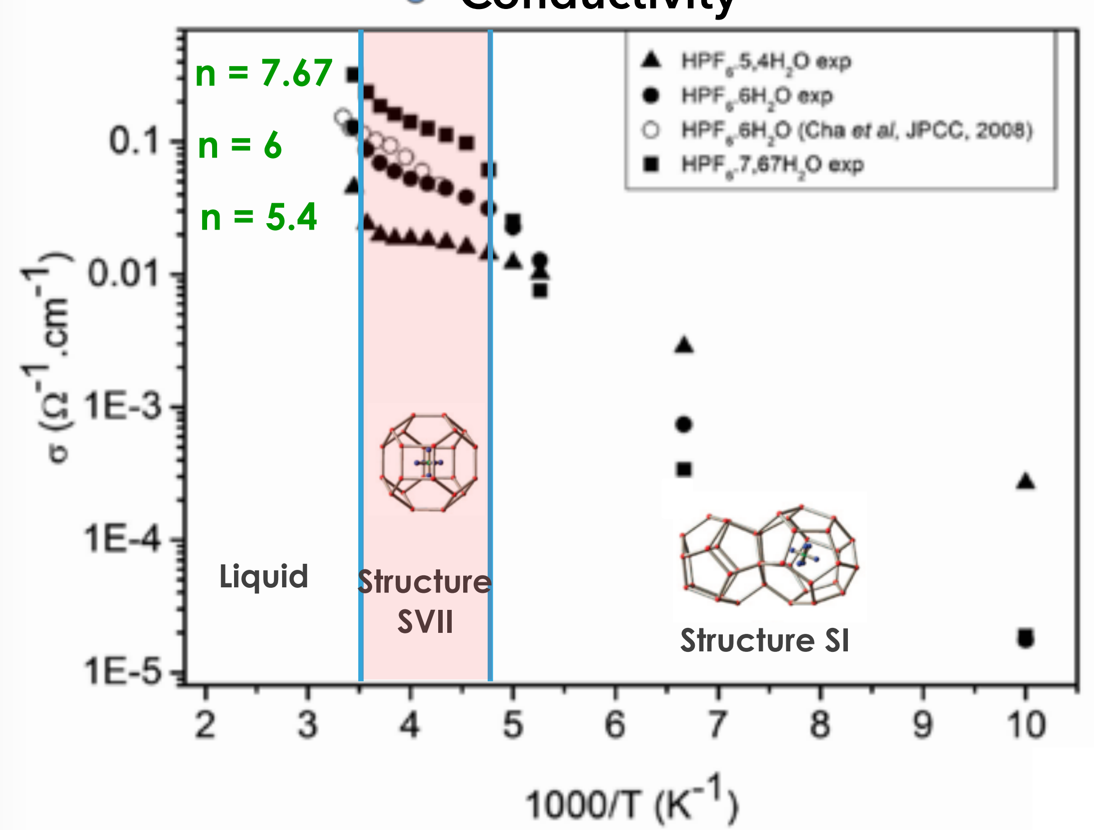
- HPF_6 hydrate: investigations by means of conductivity measurements, QENS, ^1H PFG NMR and calculations by means of *ab initio* Molecular Dynamics (MD-DFT).

Structure SVII
Cubic (a ~7.7Å)
Im3m
$2(4^6 6^8)$
1Guest - $6H_2O$

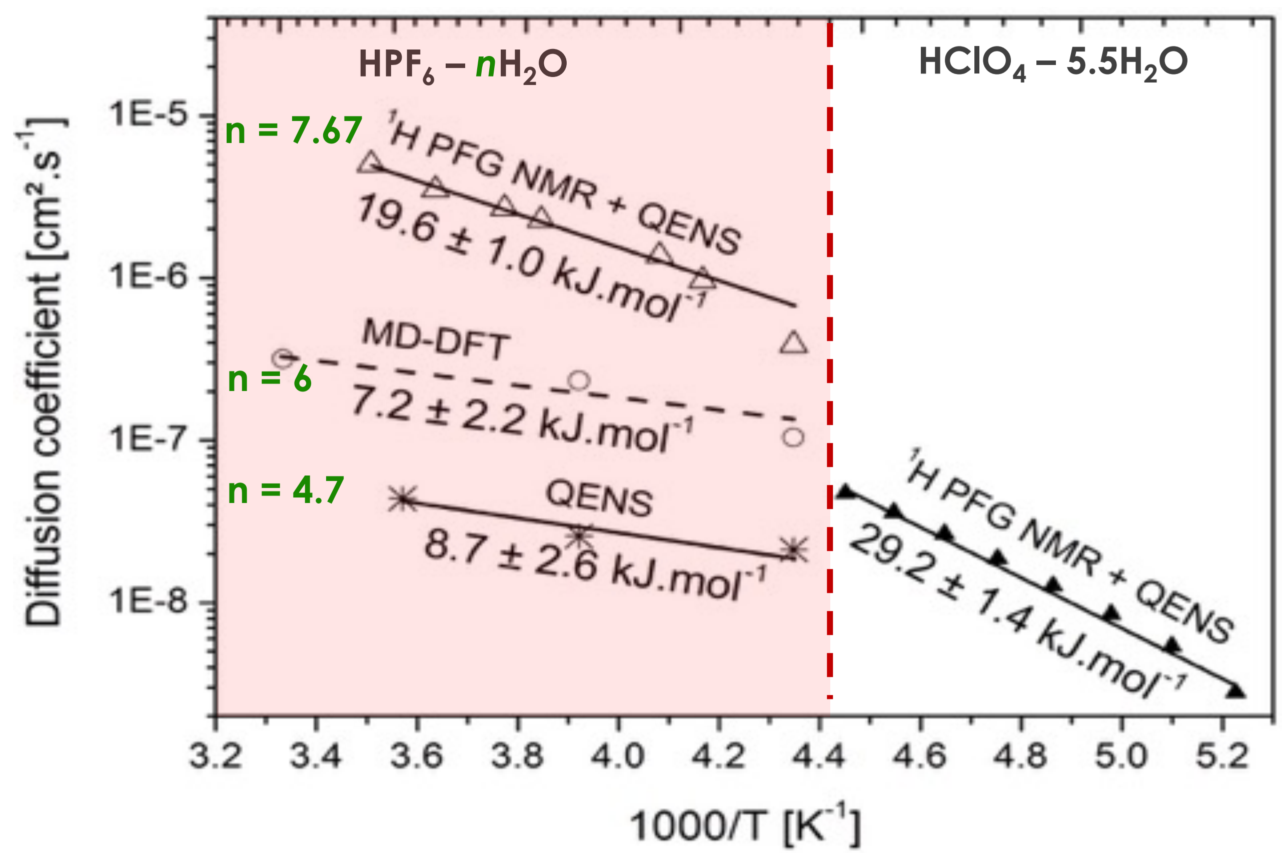


HPF_6 – nH_2O @T>230K: structure SVII whatever the hydration number n.

- Conductivity



- Diffusion coefficient



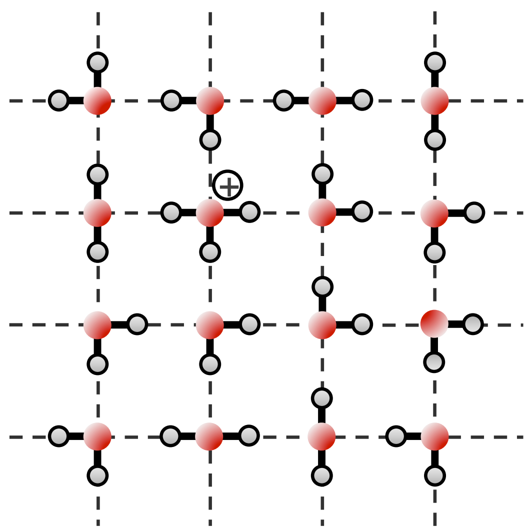
THE DIFFUSION COEFFICIENT AND THE CONDUCTIVITY INCREASE WITH THE HYDRATION NUMBER: ORIGIN?

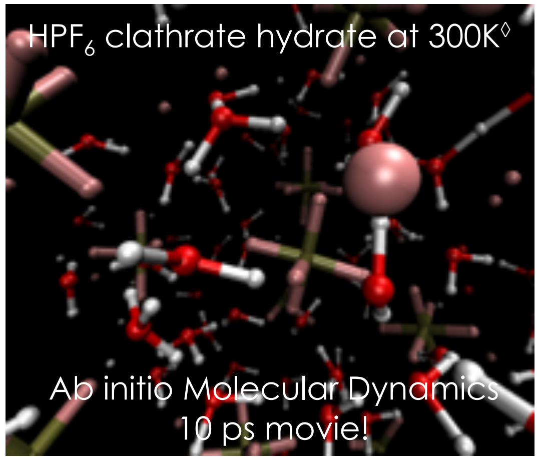
L. Bedouret *et al*, J. Phys. Chem. B 118 (2014) 13357–13364 // S. Desplanche *et al*, to be published (2020)

EXAMPLES OF APPLICATIONS

MODIFYING THE WATER DYNAMICS

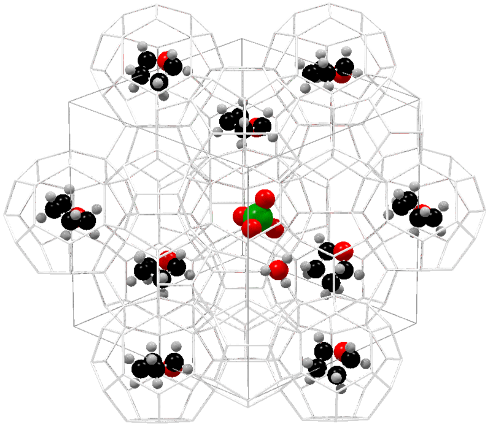
- Strong acid hydrates ($HClO_4$, HPF_6, etc.)

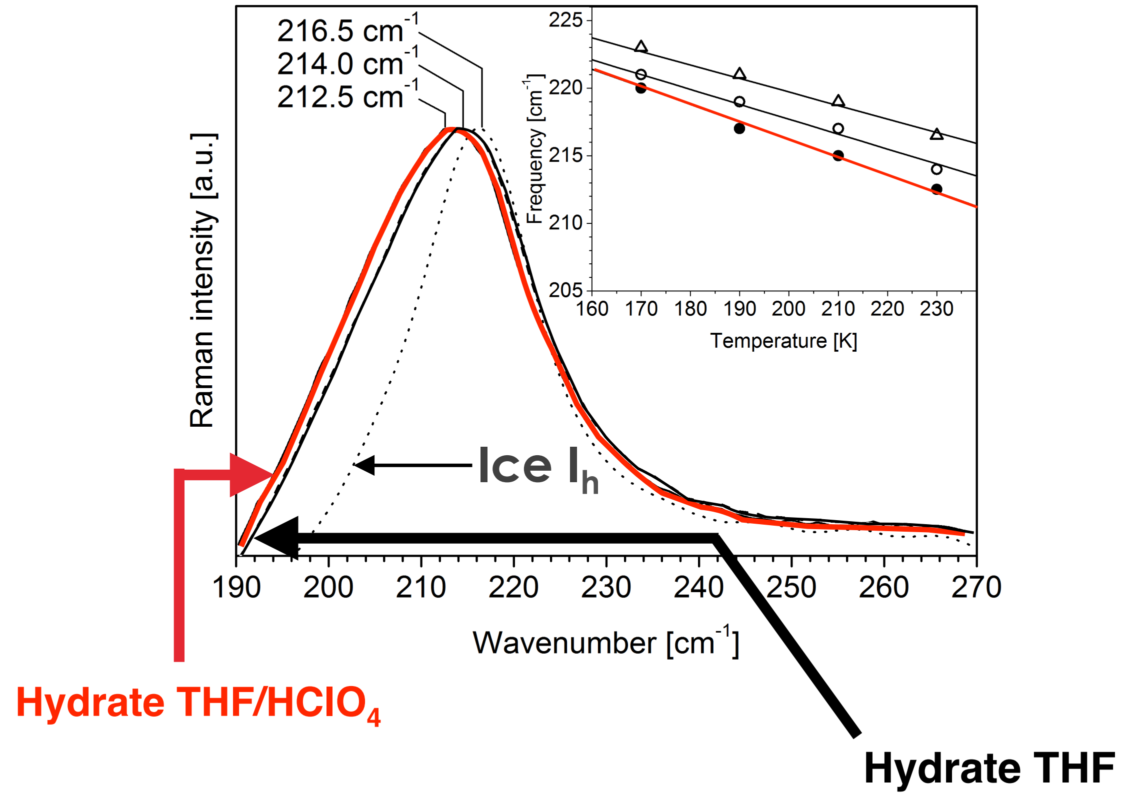




- **QENS/AIMD INVESTIGATION: « ACCELERATED » H_2O DYNAMICS IN STRONG ACID HYDRATES**
  - Ice Ih ~ ms-µs
  - Clathrate hydrate ~ µs
  - Strong acid hydrate ~ ns-ps

- Mixed THF-$HClO_4$ hydrate





- **CO-INCLUDING THF AND $HClO_4$ IN SII HYDRATE (DFT, RX)**
- **« FLEXIBILIZING » THE WATER CAGE (DFT, RAMAN)**

L. Bedouret et al, J. Phys. Chem B, (2014) / L. Bedouret et al, to be published

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

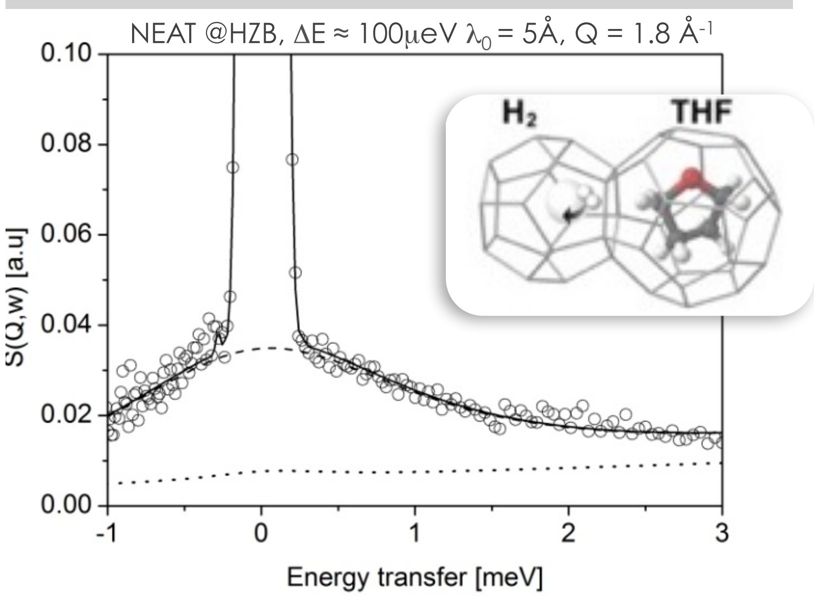
IMPACT OF ACIDIC ADDITIVES: HYDROGEN STORAGE

- Hydrogen hydrates

Formation pressure at 270K:

- H_2 Hydrate ~1000 bar
- THF/H_2 Hydrate ~100 bar

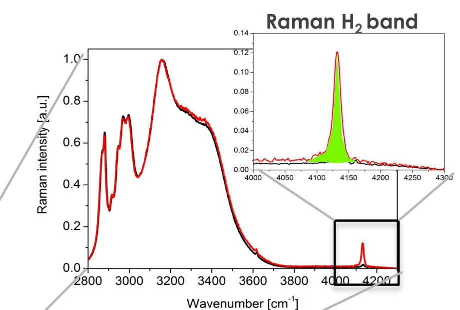
Incoherent Quasielastic Neutron Scattering (250K, 1bar)

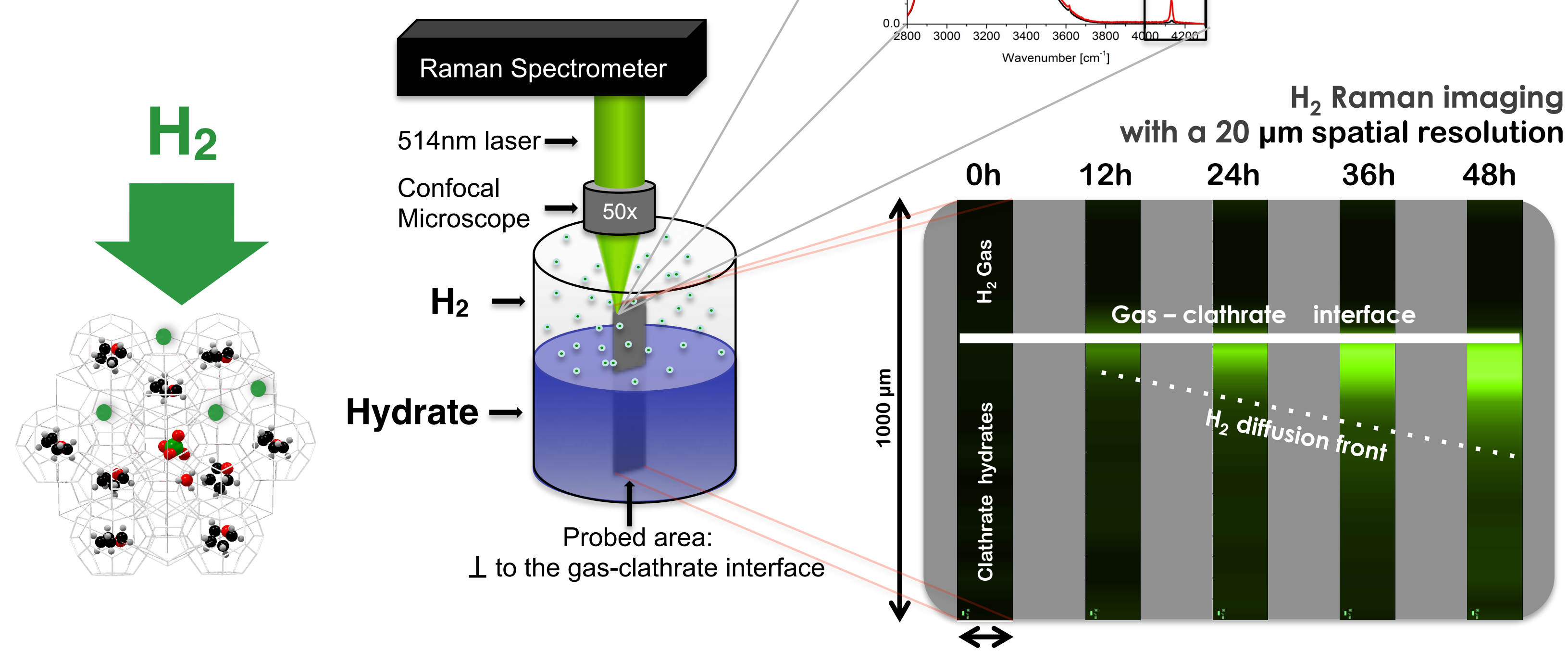


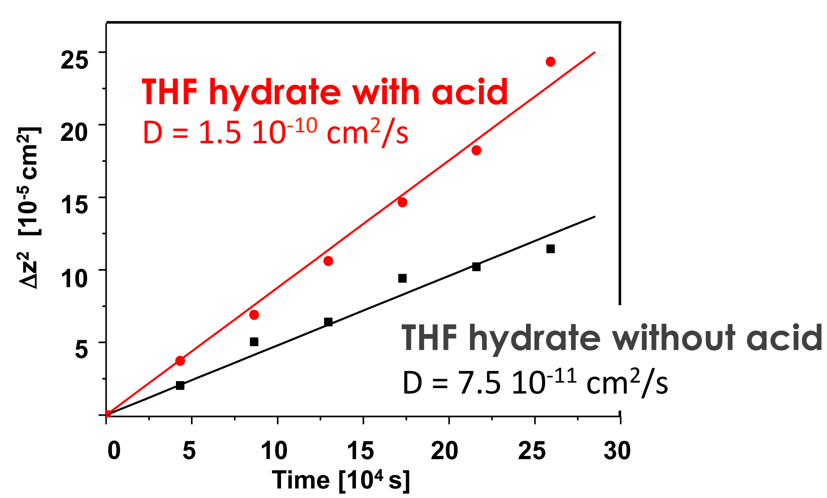
CONFINED HYDROGEN DYNAMICS: NO INTERCAGE DIFFUSION OBSERVED

FORMATION KINETICS: LONG!

- In-situ Raman imaging of Hydrogen insertion in mixed hydrate THF-$HClO_4$







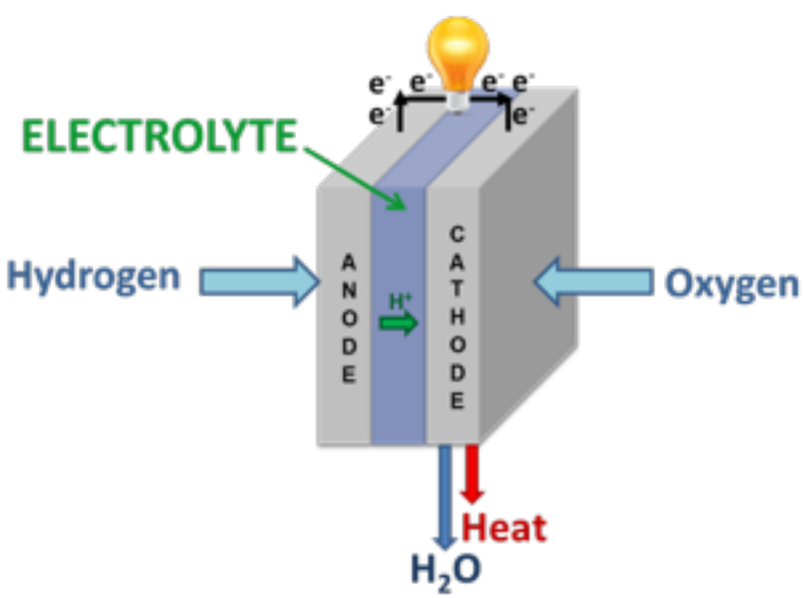
IMPROVEMENT OF HYDROGEN INSERTION (FICK BEHAVIOR) BY USING STRONG ACID ADDITIVES

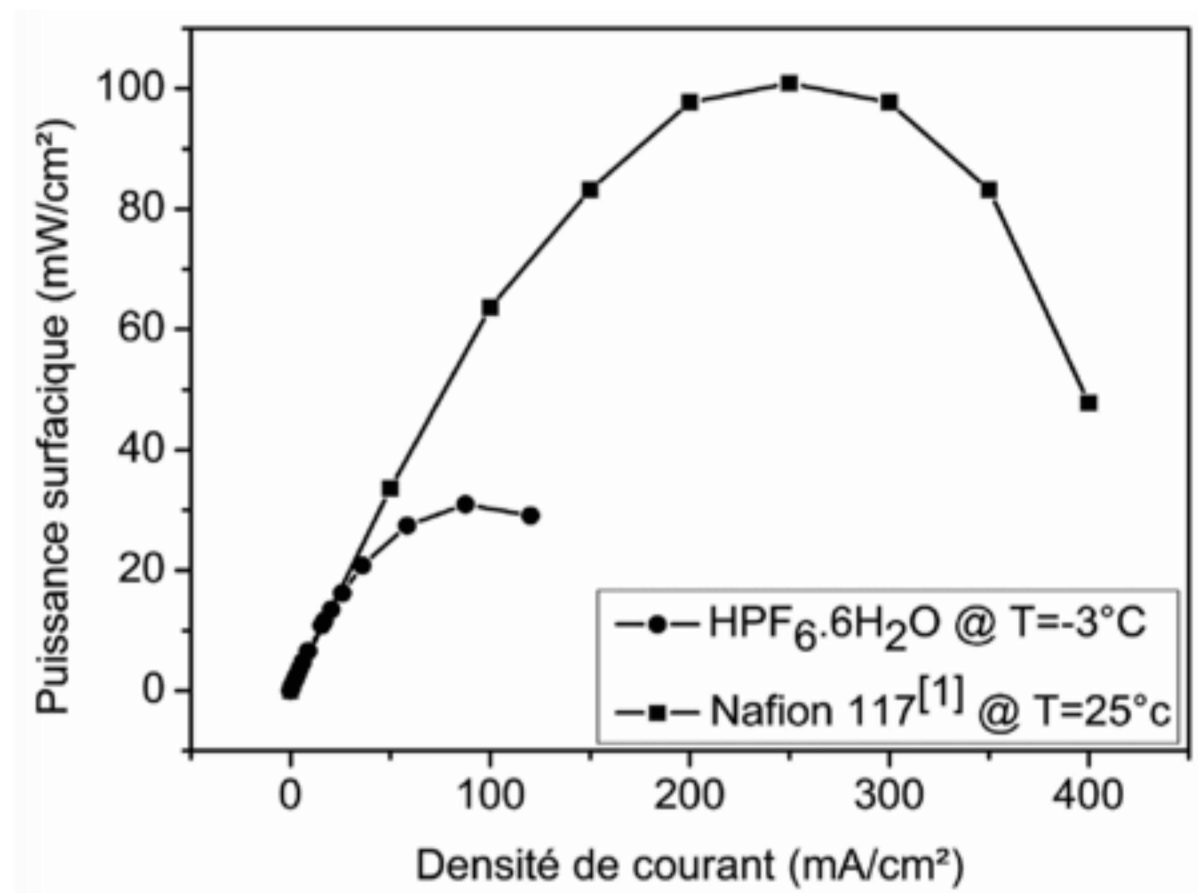
E. Pefoute *et al*, *J.Phys.Chem.C* 116 (2012) 16823

T.T. Nguyen et al, submitted to Frontiers in Chemistry (2020)

WHY NOT USING STRONG ACID HYDRATE IN A FUEL CELL?

- fuel cell design with a strong acid hydrate electrolyte and power measurement done at -3°C





THE FIRST FUEL CELL MADE OF 85% OF WATER AND WORKING BETWEEN -30°C AND +30°C!

A. Desmedt, S. Desplanche *et al*, Patent FR18 53886 (2018)

CONCLUDING REMARKS

SUMMARY

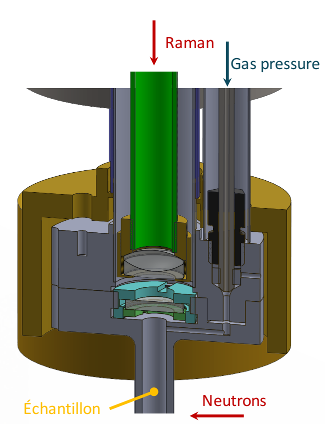
- **Gas hydrates: simple water cage for rich and complex phenomenons**.
  ➜ structural metastability ranging from days to months!
  ➜ interlinked properties: mestability / occupancy / selectivity / formation

- **Importance of structural and chemical « defects ».**
  ➜ microstructuration: improve physicochemical properties (e.g. conductivity)
  ➜ sediment analogues: geo-inspired concept for enhancing hydrate formation.
  ➜ new acidic additives: improvement of gas insertion kinetics (e.g. H_2 storage) and opportunities for new energy technologies (e.g. fuel cell)

- **Towards systems in natural environments**.
  ➜ Selective gas trapping (e.g. CO_2, CH_4, C_3H_8, etc) and issues regarding the estimation of natural gas hydrates
  ➜ Natural gas hydrates in the Black sea (cruise in July 2020) Ifremer
  ➜ Gas hydrates formation on Titan NASA

NEUTRON AND MORE

- **Neutron scattering**: a unique tool for gas hydrates sciences, …especially in combination with other techniques.
- **Development of correlative measurements (e.g. dielectric, NMR, X-ray, Raman, IR, etc.)**
  - Raman / Neutron: Adapted for orange cryostat and numerous neutron instrument (spectroscopy AND diffraction)
  - Several incident wavelengths (to avoid fluorescence)
  - High-pressure sample cell: crucial for following in-situ formation of gas hydrates, but not only!



- F. Adamietz, D. Talaga, J.L. Bruneel, A. Desmedt
- A. Helary, C. Alba-Simionesco

THANK YOU
FOR YOUR ATTENTION