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Study of High Pressure CO_2 Clathrates Hydrates on Ganymede

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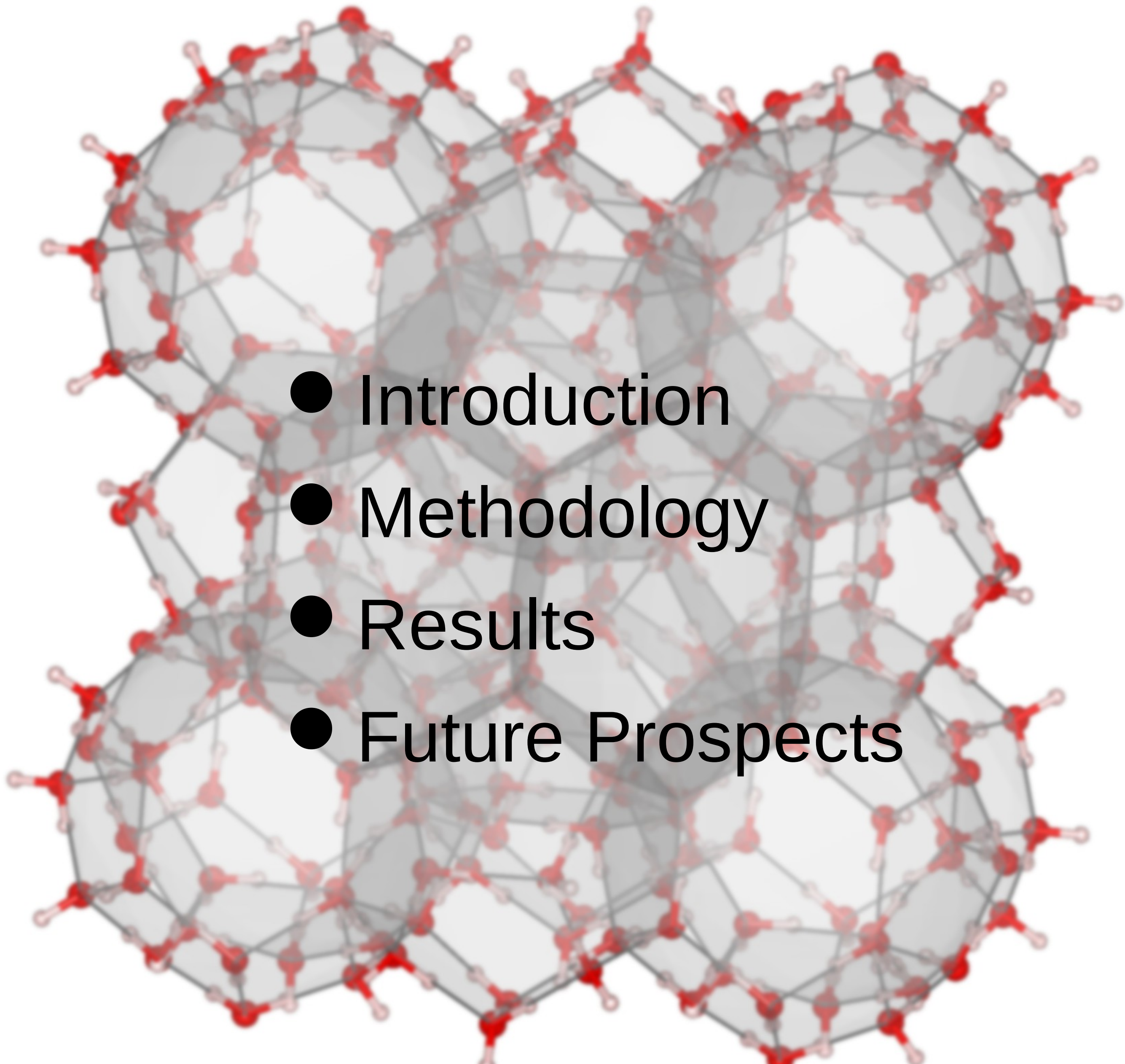
Outline



- Introduction
- Methodology
- Results
- Future Prospects

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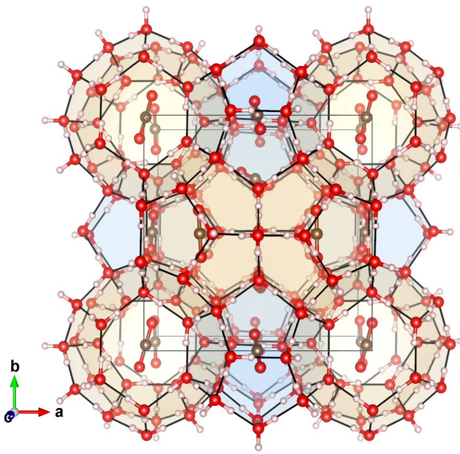
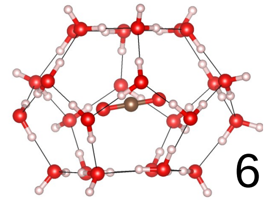
Introduction: Ganymede

- Jupiter Icy Moon
- H_2O, salts and CO_2
- Liquid water in internal reservoirs
- Low Temperature: from 110 to 300 K
- High Pressures: up to 1.3 GPa
- Appropriate conditions for hydrate synthesis
- Need of easy ways to recognize clathrates

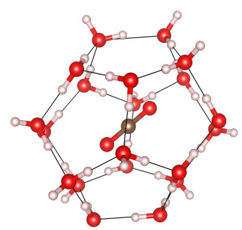
Introduction: Clathrates

sI





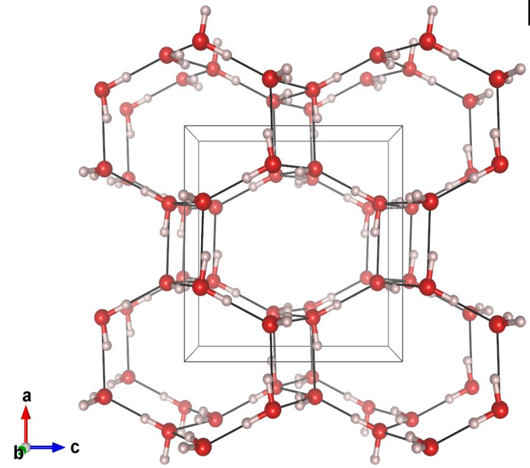
6 x $5^{12}6^{2}$
H cage, big



2 x 5^{12}
P cage, small

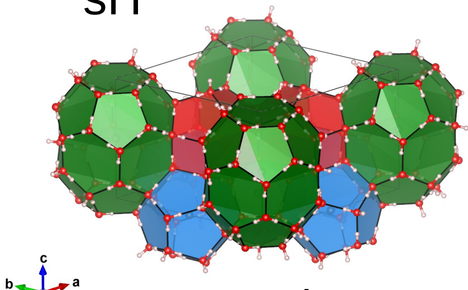
Cubic
46 H_2O per u.c. / 8 cages

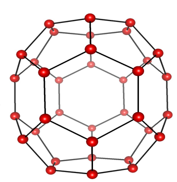
FIS



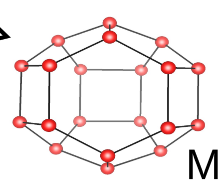
Orthorhombic
8 H_2O per u.c.
Channels
Up to 4 guests

sH





1 x $5^{12}6^{8}$
Big cage

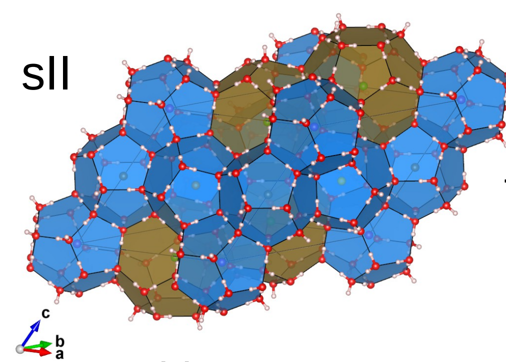


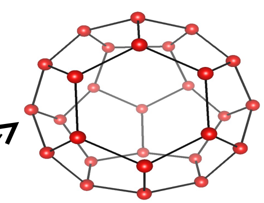
2 x $4^{3}5^{6}6^{3}$
Medium cage

3 x 5^{12} Small (P) cage

Hexagonal
34 H_2O per u.c.
6 cages

sII





8 x $5^{12}6^{3}$
Big cage

16 x 5^{12}
Small (P) cage

Cubic
136 H_2O per u.c.
24 cages

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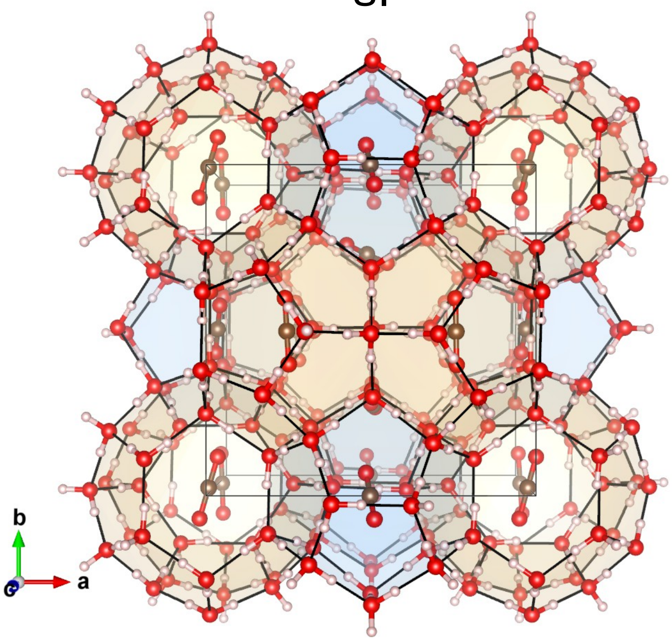
Introduction: Clathrates

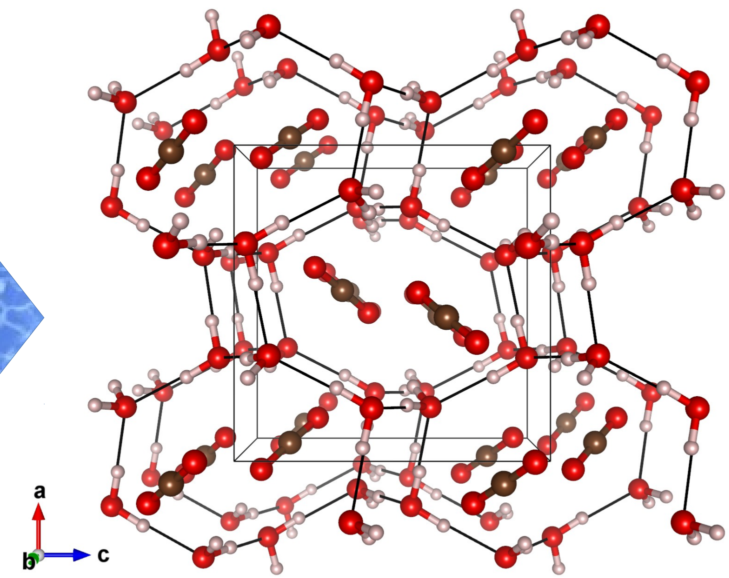
sI



0.7 GPa

T independent

HP phase (FIS)



Latest experiments show HP phase transition and then decomposition around 1 GPa

Structural studies show lack of the usual sI → sH → FIS progression

Bollengier, O. et al. *Geochim. Cosmochim. Acta* **119**, 322 (2013)
Tulk, C. A. et al. *J. Chem. Phys.* **141**, 174503 (2014)

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Methodology

DFT *ab initio* calculations

Periodic boundary conditions and molecular cluster calculations

GGA functional (PBEPW86)

XDM treatment of VdW interactions

↓

Energetic stability

Equation of state (EOS)

Vibrational frequencies

MALTA Supercomputing center

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Results: Structure

sI Lattice parameter: 11.75 Å (11.83 Å at 77 K)

FIS Lattice volume: 359.6 $Å^3$ (291.3 $Å^3$ at 173 K)
FIS Lattice parameters(Å): a=7.92, b=5.73, c=7.92

sI Vinet EOS and polyhedral decompositon

	B_0(GPa)	B_0'
Full structure	16.3	1.87
H cages	16.2	1.84
P cages	16.7	1.88

Vinet EOS:

$$3B_0\left(\frac{1-x}{x^2}\right)e^{\frac{3}{2}(B_0')(1-x)}$$

$$x=\sqrt[3]{\frac{V}{V_0}}$$

Clathrates are very compressible materials
but tougher than pure ice Ih (B_0~8 GPa*)

H cages more compressible than P

* D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water* (1969). Chapter 3

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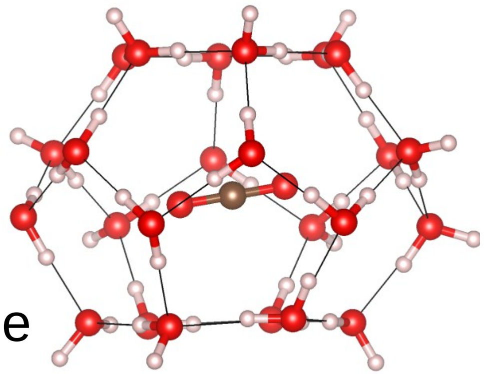
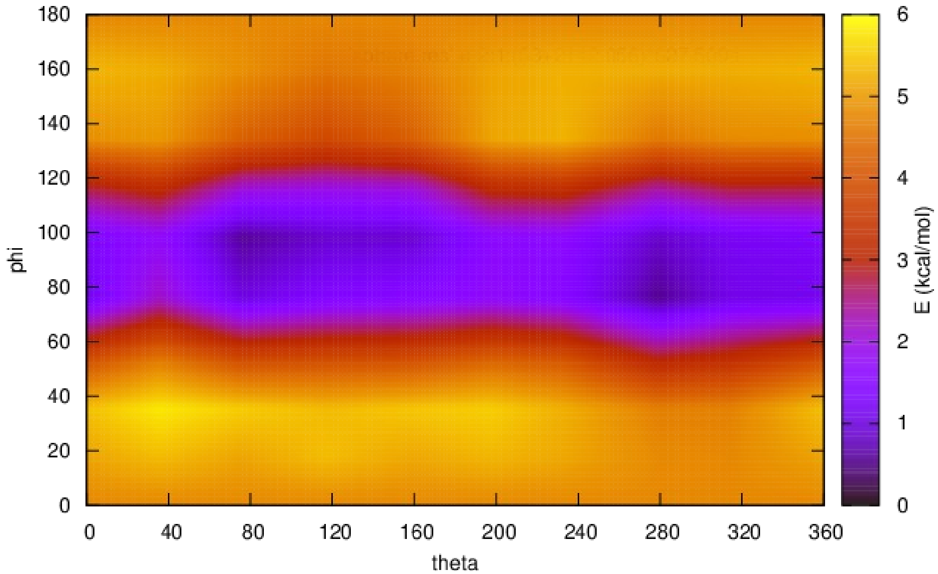
Results: CO_2 orientation

sI structure

H cage



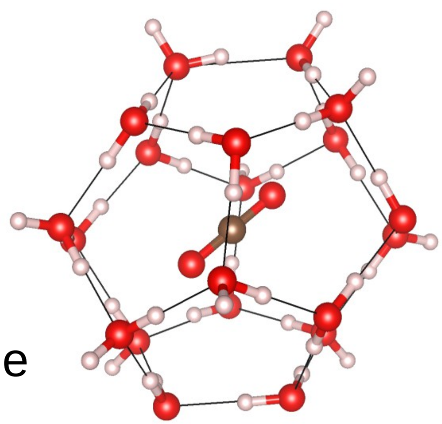


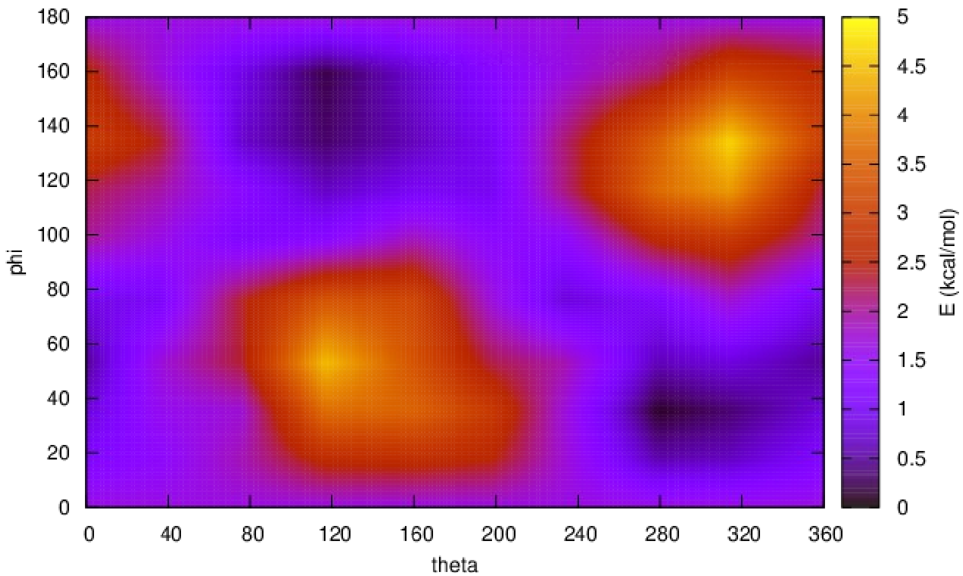
Stable position perpendicular to hexagons

Free rotation in a plane

Libration in the perpendicular axes

P cage





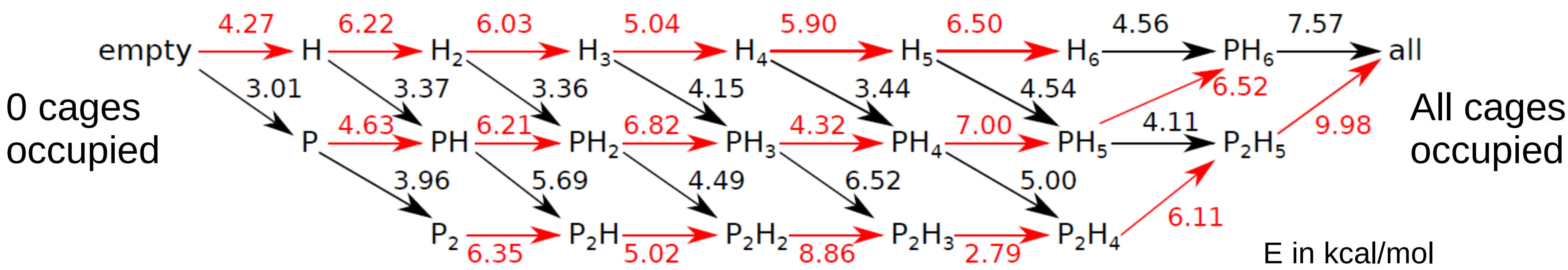
Stable position perpendicular to a pentagonal face

Fernando Izquierdo-Ruiz

Results: Occupation

sI structure

P_xH_y: x and y → number of cages occupied



H cage occupation energy released = 6 kcal/mol

P cage occupation energy released = 4.6 kcal/mol

Total occupation energy released = 46 kcal/mol

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Results: Frequencies

P(GPa)	SS_P	SS_H	AS_P	AS_H	B_w	S_w
Free	1282		2283		1619	3618/3793
0.036	1368	1358	2433	2422	1674 – 1818	3053 – 3513
0.332	1370	1358	2438	2421	1678 – 1820	3038 – 3509
0.617	1369	1358	2436	2421	1675 – 1823	3001 – 3499
0.946	1370	1360	2437	2424	1670 – 1827	2981 – 3486

sI relevant vibrations. Freq. in cm^{-1}, SS=Symm. Stretching, AS=Antisymm. Str., B=Bending, S=Stretching

CO_2 frequency blue shift upon encapsulation

Bigger in P cages

P does not affect CO_2

Broadening of H_2O bending

Red shift in H_2O stretching

sI H cage libration

Torsional harmonic oscillator model: $E = \frac{1}{2} k \varphi^2 \quad k = \frac{\partial^2 E}{\partial \varphi^2}$

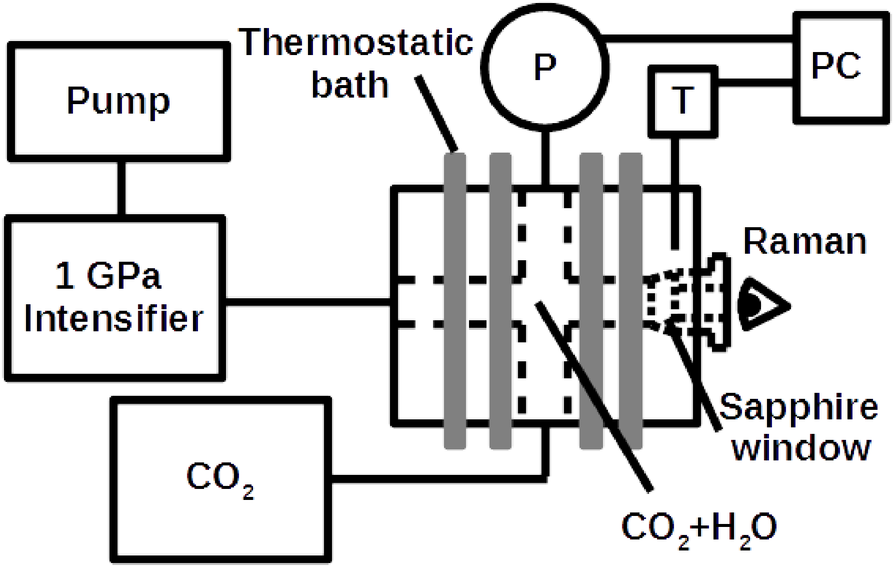
$$\check{\nu}(cm^{-1}) = \frac{1}{2\pi c}\sqrt{\frac{k}{I}}$$

I: Moment of inertia of the guest molecule

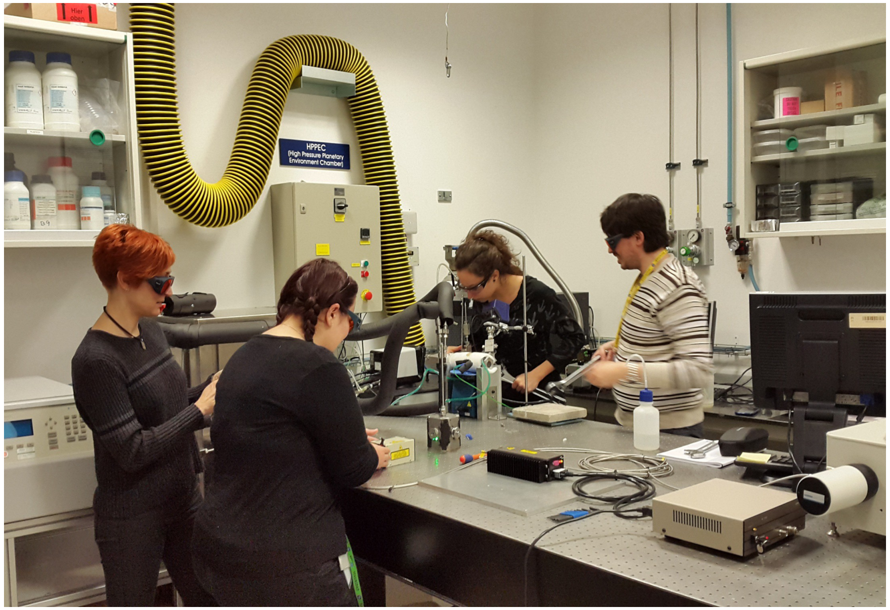
Averaged value over several energy profiles at different θ angle

$$\check{\nu} = 45\ cm^{-1}$$

Present Developments & Future Prospects



Very High Pressure Planetological chamber (VHPPC)



Finnish the set up of the VHPPC
Prepare Sapphire Anvil Cell experiments

Experimental study of both low and high pressure phases of CO_2 hydrate

Further theoretical calculations on FIS and other possible CO_2 hydrate structures

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Thank You

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QUIMAPRES

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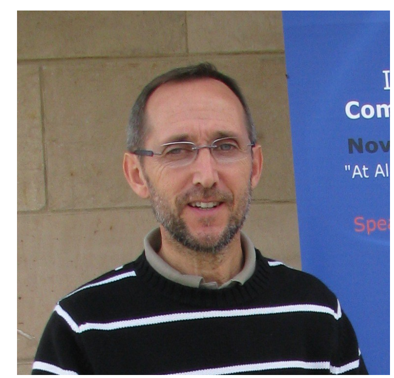
Matter at High Pressure

O. Prieto-Ballesteros



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