High capacity molecular hydrogen storage in novel crystalline solids

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Geert-Jan Witkamp & Hugh Docherty

TUDelft VANDERBILT

Hydrogen Storage

Requirements:

1. High hydrogen content (by mass and volume)
2. Moderate *P-T* storage
3. Easy hydrogen release
4. Environmentally friendly by-products
5. Cost and availability
6. Safety

GCEP Exploratory Project

1. Discovery at high pressures and variable temperatures

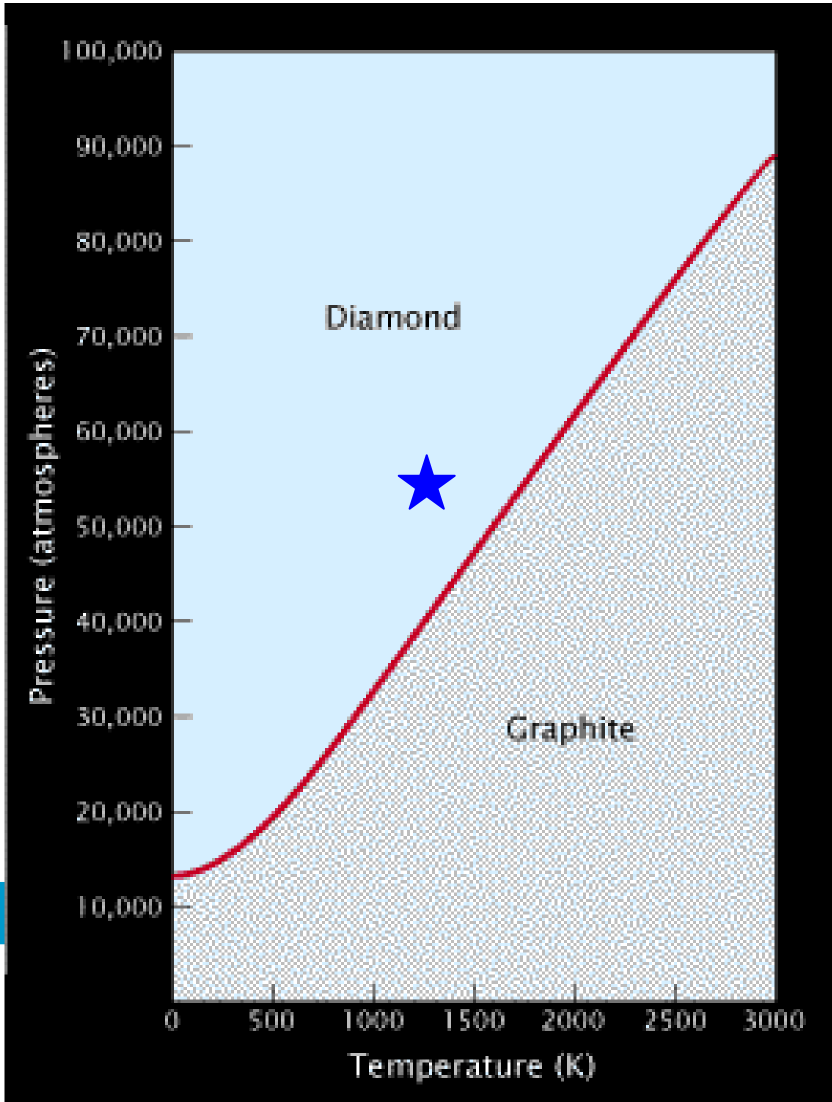
- Use coupled experimental and theoretical approach to search extended pressure-temperature range
- Study how promising phases store hydrogen (i.e. determine structure and bonding)

2. Recovery and synthesis at practical conditions

- Explore pathways to synthesize these materials near ambient conditions
- Investigate chemical promoters for stabilizing the structure

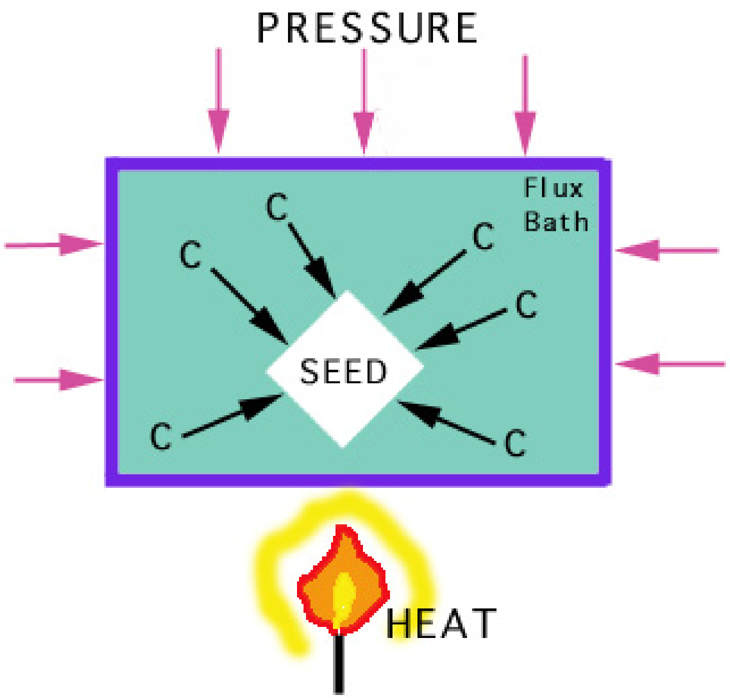
High pressure for practical applications?

- Stable form of carbon at the Earth's surface is graphite
- Diamonds are formed at high pressure and temperature within the Earth
- They are metastable when brought quickly to room temperature and pressure in kimberlite pipes



High Pressure-High Temperature diamonds

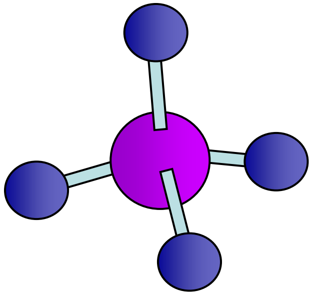
- HPHT method uses carbon source + seed crystal + catalyst
- These are kept in a vessel at:
  - High pressure → 5.5 GPa, 55,000 bar
  - High temperature → >1500°C
  - Time (days)

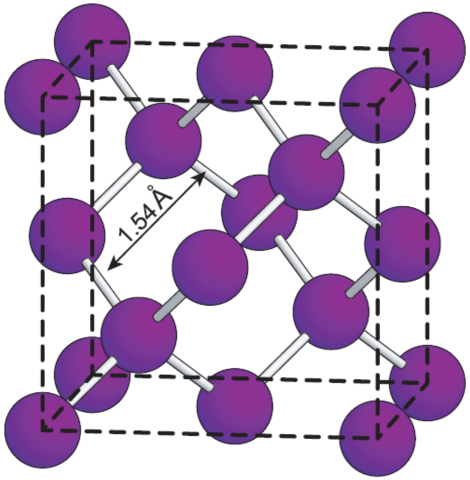


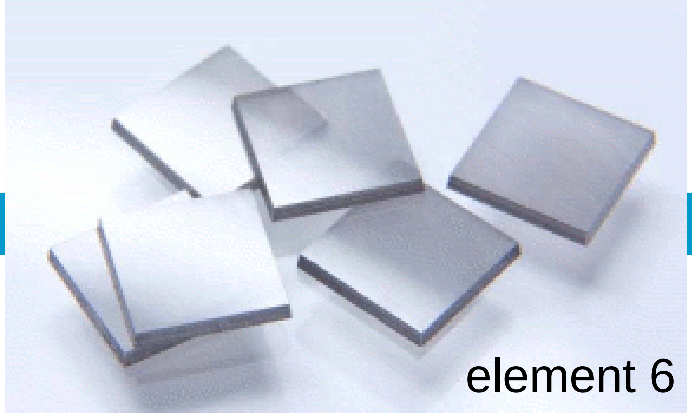
DeBeers

Chemical vapor deposition

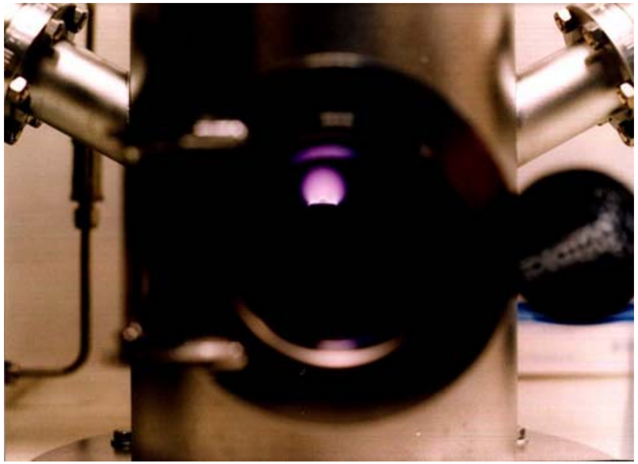
- Use knowledge of bonding in diamond to synthesize this high pressure phase at low pressure
- CVD uses near vacuum conditions to grow diamond from a methane plasma on a diamond substrate: $CH_4 \rightarrow C + 2H_2$
- Tetrahedral bonding of carbon in methane mimics diamond






element 6

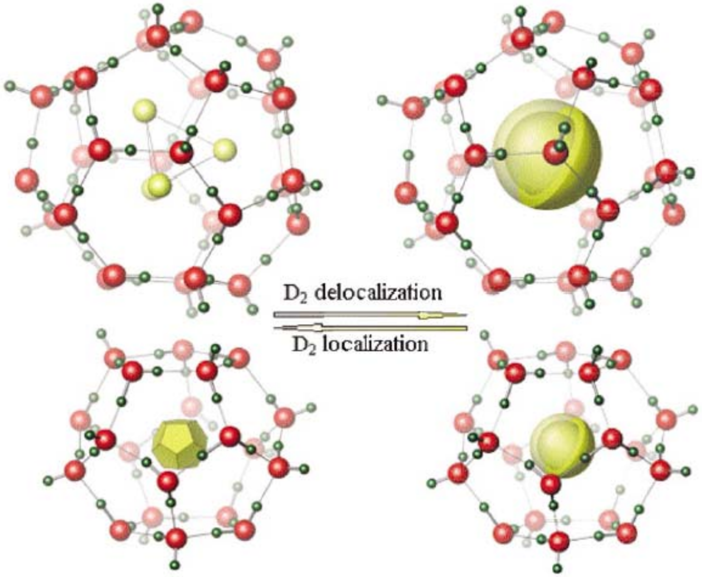
Diamond Growing in a Plasma Reactor



Example: H_2+H_2O system

- H_2 clathrate, $H_2(H_2O)_2$, with sII structure found at high pressure (2 kbar) and low temperature (240 K)
- Can be quenched to ambient pressure with low temperature (77 K)
- Chemical stabilization of sII structure
- Reduced hydrogen storage, kinetics?
- Demonstration of approach
  - ➢Search for promising phases over broad *P-T*
  - ➢Determine structure
  - ➢Synthesis at more practical conditions

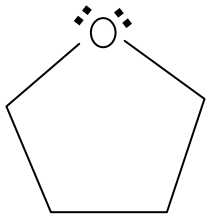
Methane clathrate



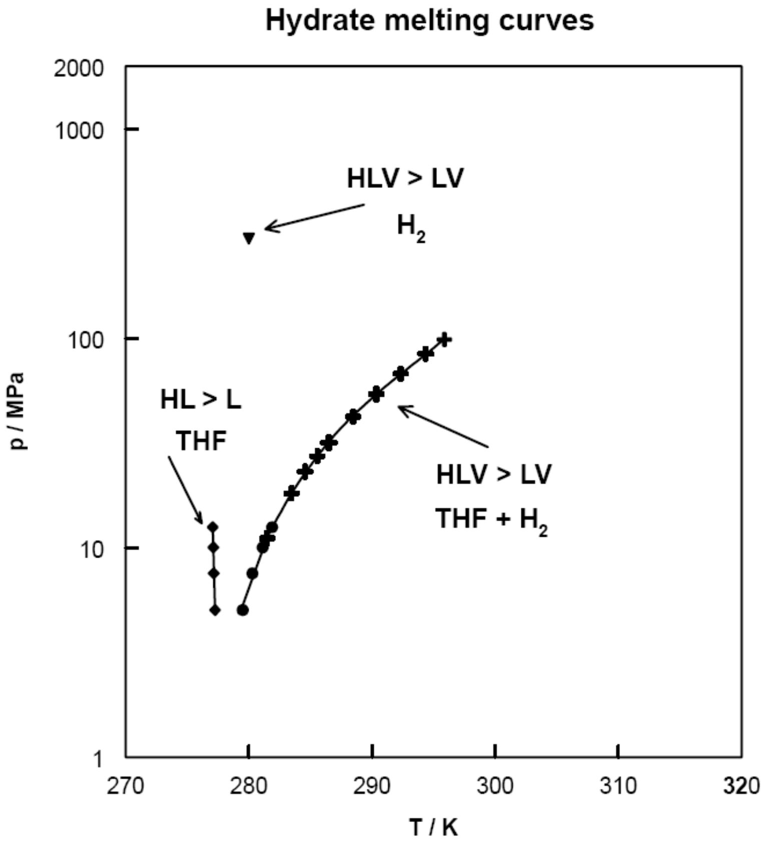
W. Mao *et al*, Science 2002
Lokshin *et al*, PRL 2004

Chemical stabilization

- Use THF as a promoter molecule to fill large cage in sII clathrate structure
- Forms mixed THF + H_2 clathrate at 277.3 K at ambient pressure
- H_2 content reduced by addition of THF



Tetrahydrofuran (THF)



Florusse *et al*, Science 2004
Lee *et al*, Nature 2005

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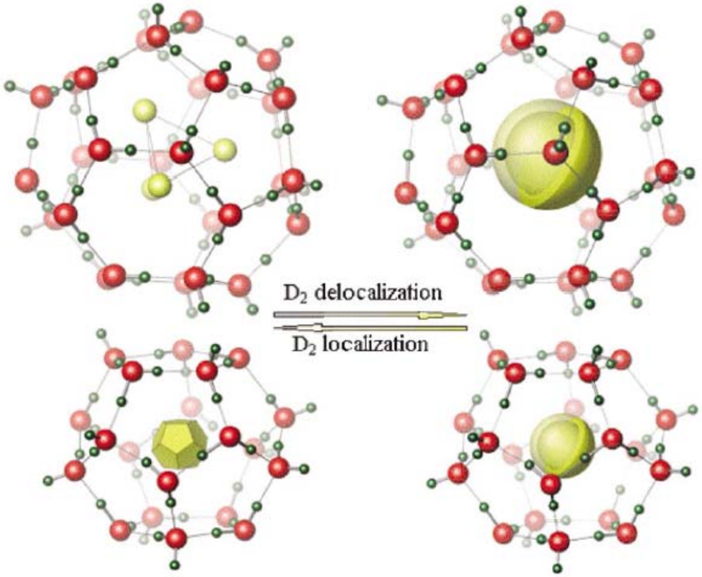
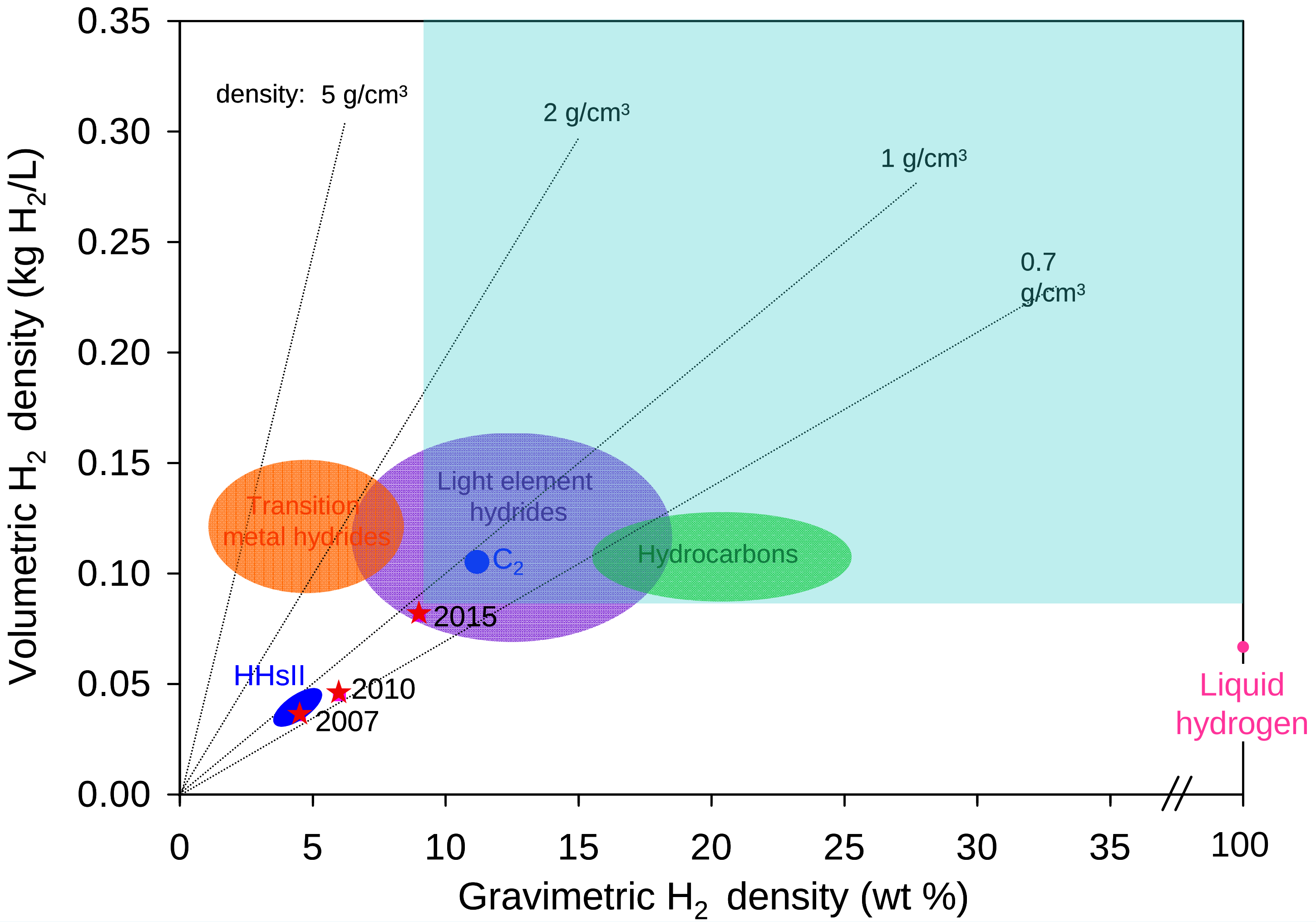


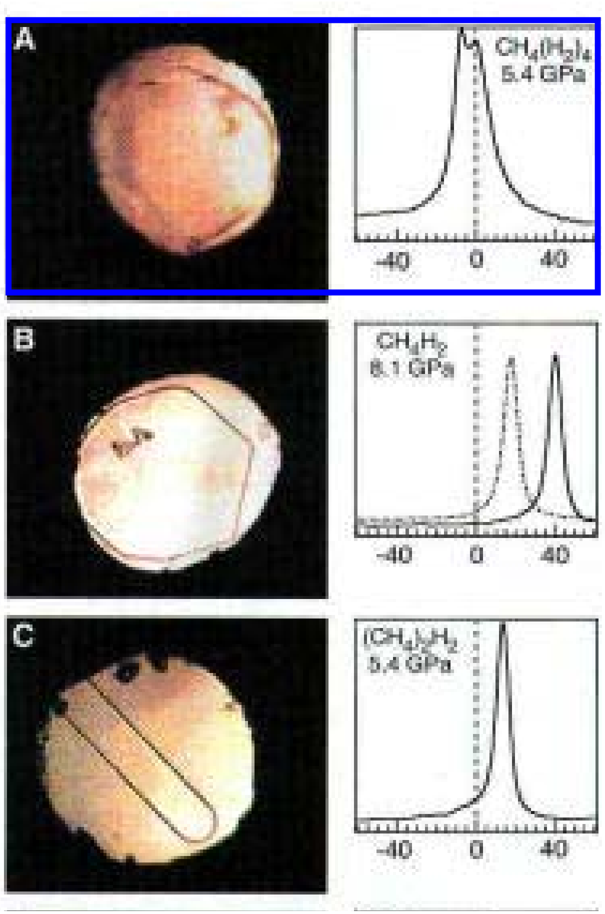
W. Mao *et al*, Science 2002
Lokshin *et al*, PRL 2004

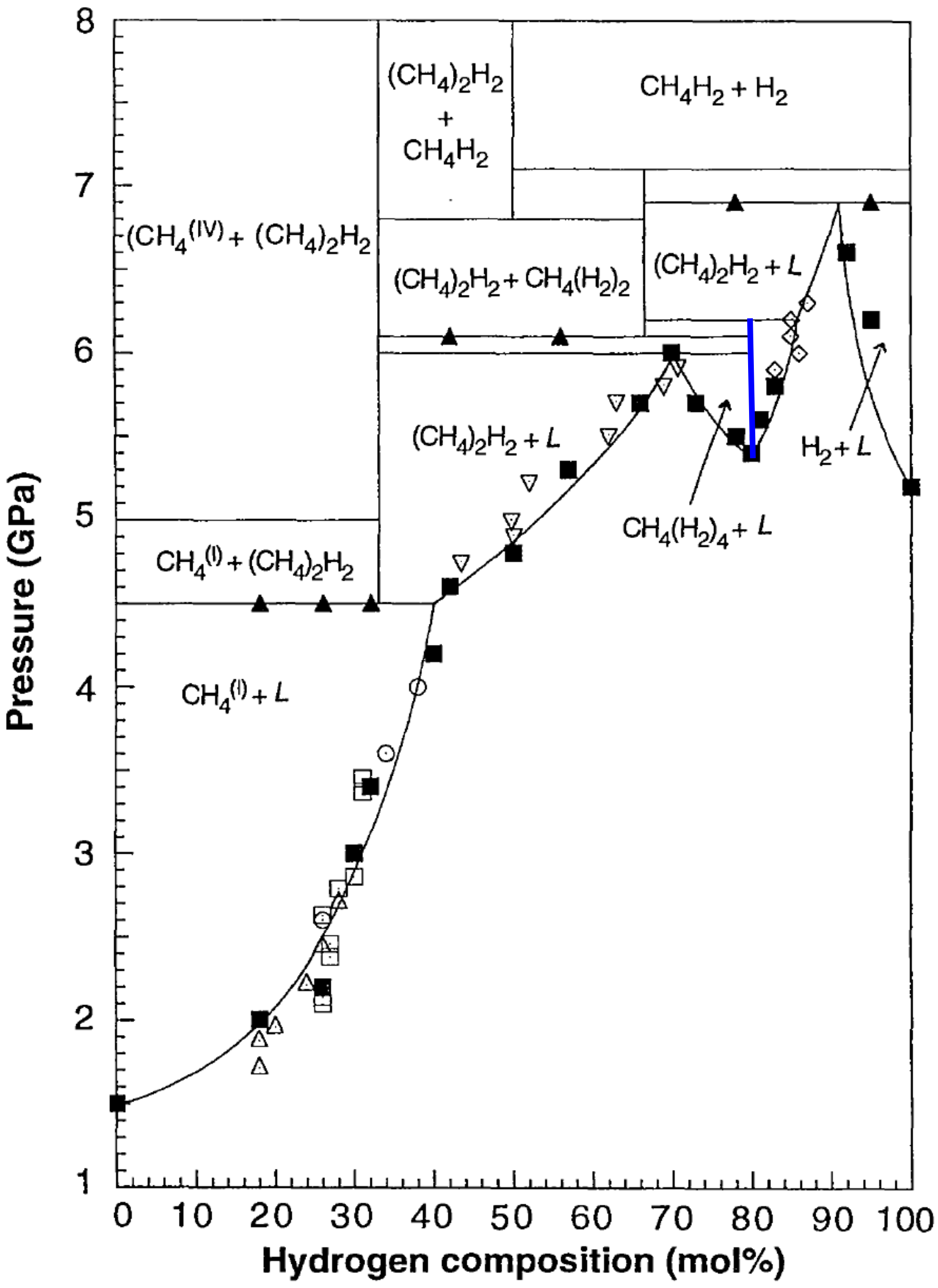
Hydrogen Storage Capacity



W. Mao *et al*, Physics Today 2007

CH_4 + H_2 system

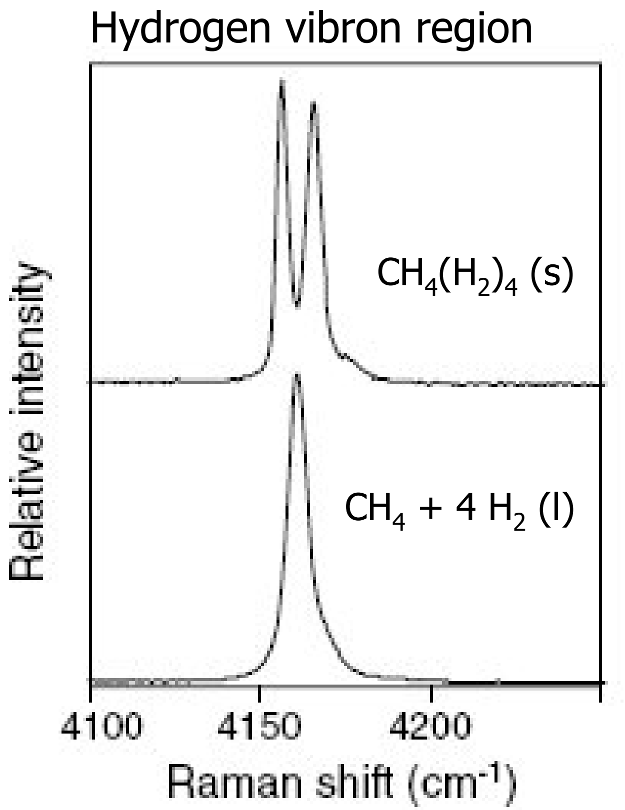




M. S. Somayazulu *et al*, Science 1996

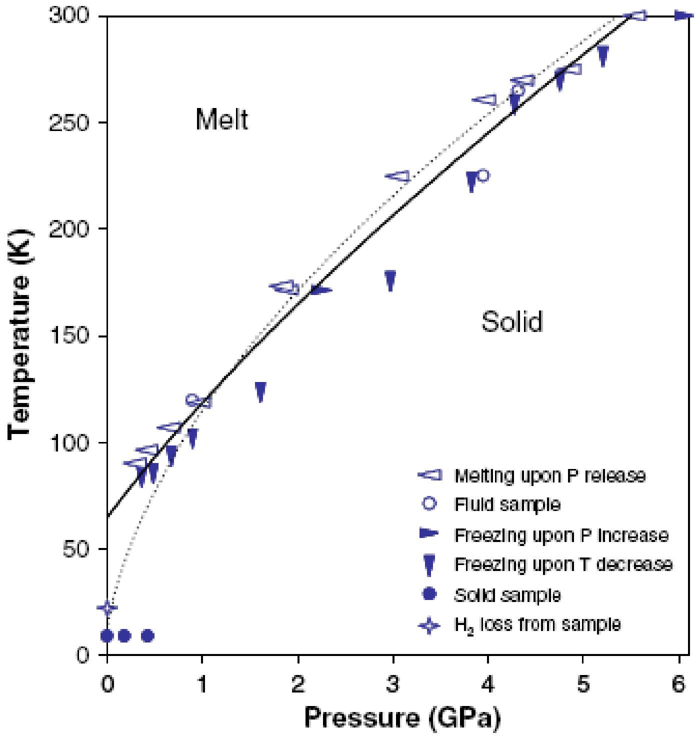
$CH_4(H_2)_4$

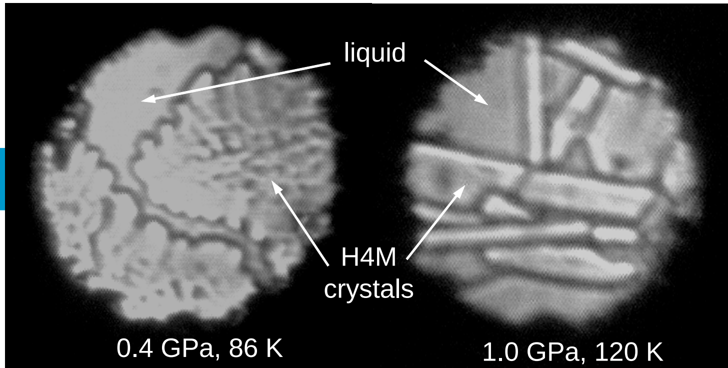
Raman spectroscopy:



2 hydrogen sites?

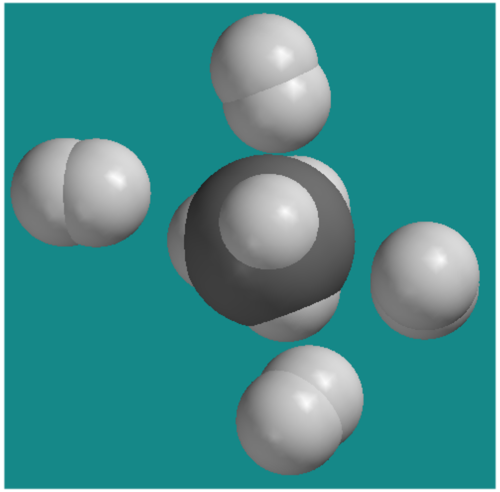
Melting curve:





W. Mao *et al*, CPL 2005

$CH_4(H_2)_4$



- 33.4 wt% molecular hydrogen
- 50.2 wt% total hydrogen
- Stable at high pressures or low temperature
- Unknown structure

Structure determination of $CH_4(H_2)_4$

- Experimental (XRD, Raman spectroscopy)
- Theory (NPT-classical models, DFT-calculations)

→ Insight into H_2 interactions with host materials

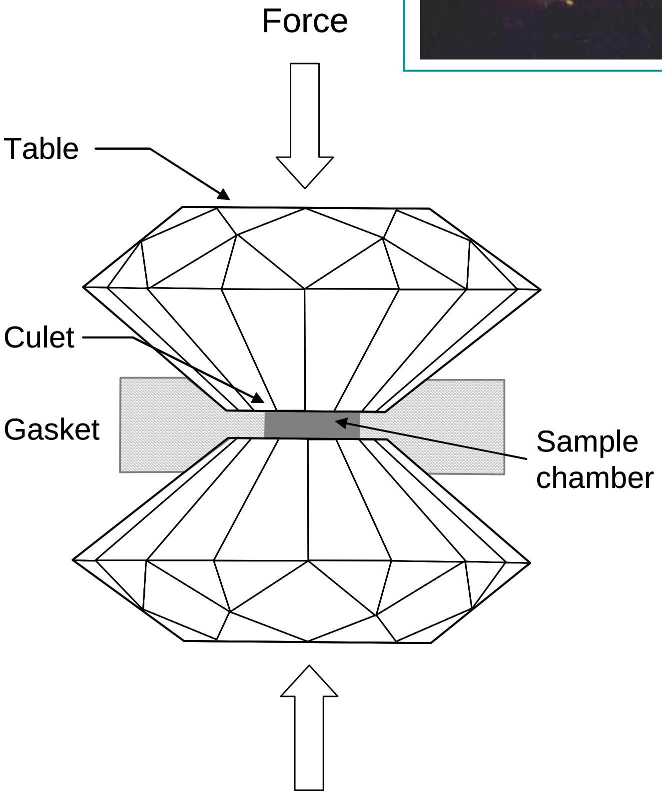
→ Design of optimized hydrogen storage material

Experimental techniques

Diamond anvil cell:

- Explore large *P-T-x* space

  (ambient – 500 GPa, mK – 5000 K)
- Transparent to large range of E-M radiation
- Sample size < 0.001 mm^3



Force

Table

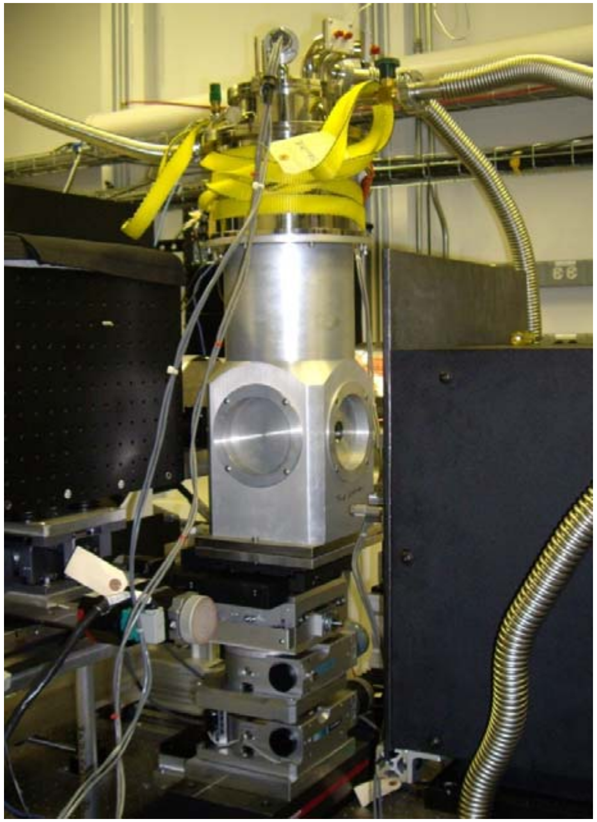
Culet

Gasket

Sample chamber

$CH_4(H_2)_4$ diffraction

Mounting cell in cryostat



On-line cryostat

$CH_4(H_2)_4$ crystals
at 3 GPa and 150 K

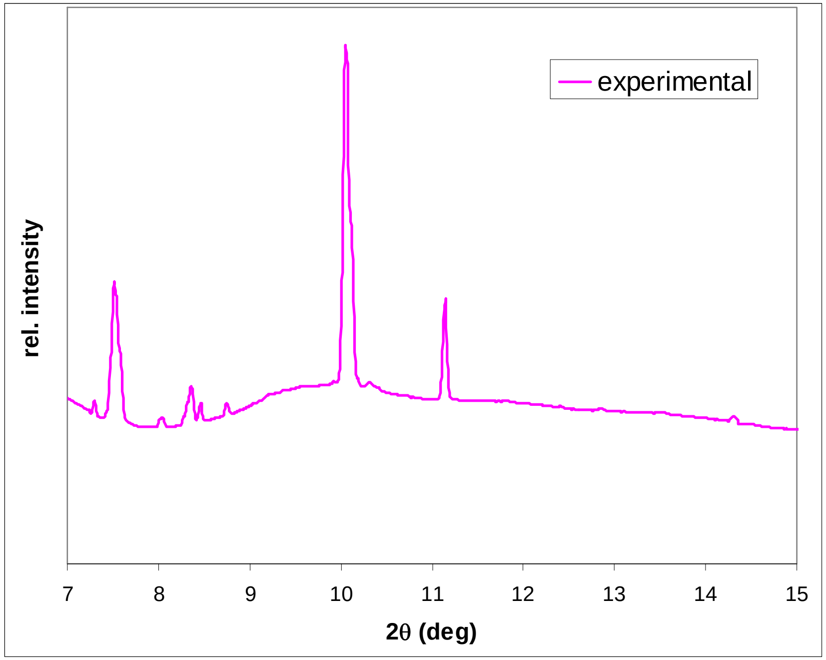
HPCAT, 16-IDB, Advanced Photon Source, Argonne National Laboratory

Experimental structure determination

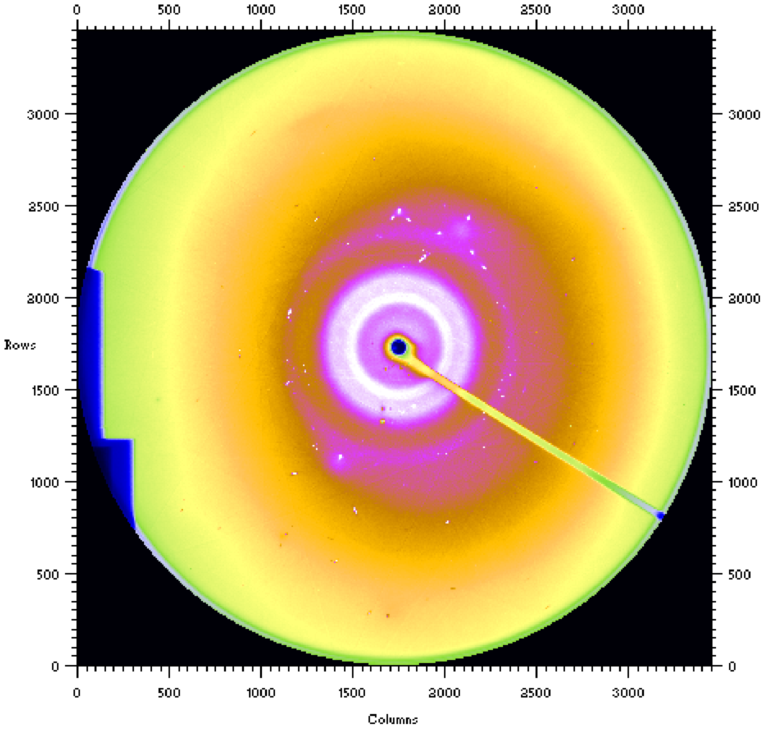
X-Ray Diffraction:

- Coarse polycrystal
- Can constrain unit cell symmetry
- Can not refine atomic positions

T = 200 K, p = 3.5 GPa



($\lambda = 0.40747$ Å)

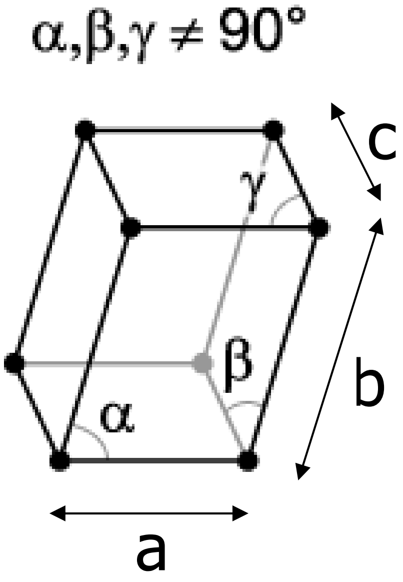


Theoretical structure determination

Step 1: Generation of Multiple Initial Configurations:

→ Generation of 1.1×10^{11} Random Triclinic (Unit) Cells

→ 1100 runs of 1×10^8 configurations each



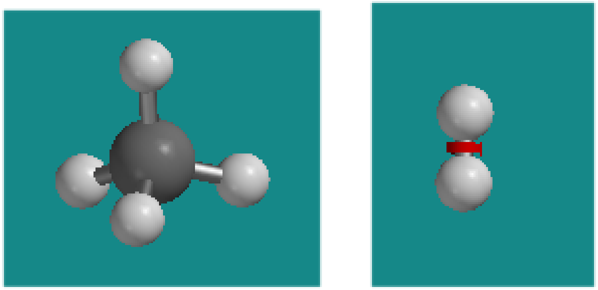
- Fixed T, p, N_i
  (298 K, 5.8 GPa, 16 H_2 and 4 CH_4)
- Randomly selected ρ, α, β, γ, a, b, c
  $0.75 \cdot \rho_{expected} < \rho < 1.25 \cdot \rho_{expected}$
  $55^o < \alpha, \beta, \gamma < 125^o$
  $0.5 < b/a, c/a < 1.5$
- Random insertion of atoms N_i

Theoretical structure determination

Step 2: Fast screening using classical molecular models

SPC model:

- 1 Lennard-Jones site
- 3 (hydrogen) or 5 (methane) point charges



→ 1100 most favorable configurations (one from each run)

→ Orthorhombic unit cell (V = 372 Å^3)

J. S. Tse *et al*, J. Chem. Phys. 1984

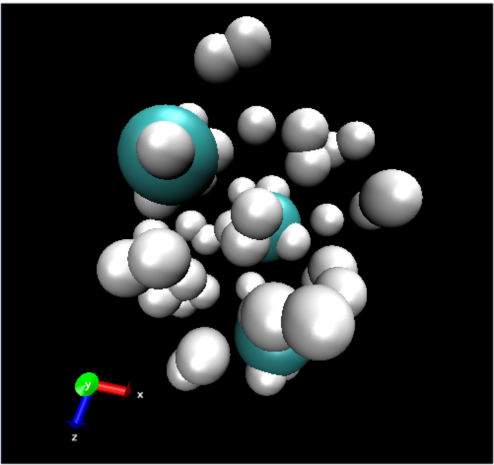
S. Alavi *et al*, J. Chem. Phys. 2005

Theoretical structure determination

Step 3: Geometry optimization using ReaxFF

- Input: 100 most favorable configurations from Step 2
- Use of bond orders
- Continuous breaking/forming of bonds

- Lowest energy configuration
  →Orthorhombic unit cell (V = 333 Å^3)

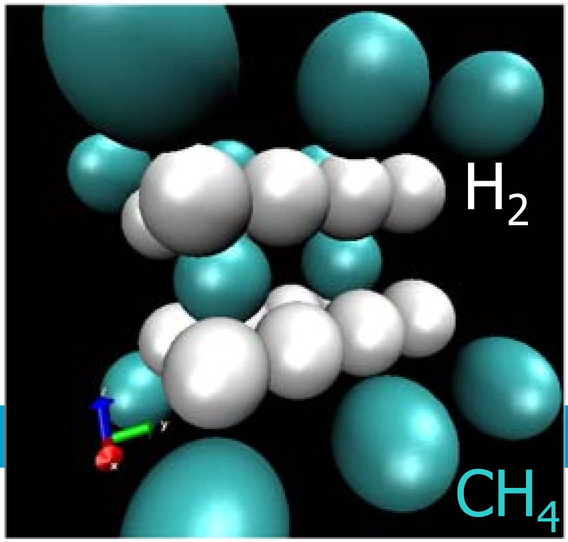


A. C. T. van Duin *et al*, J. Phys. Chem. A 2001

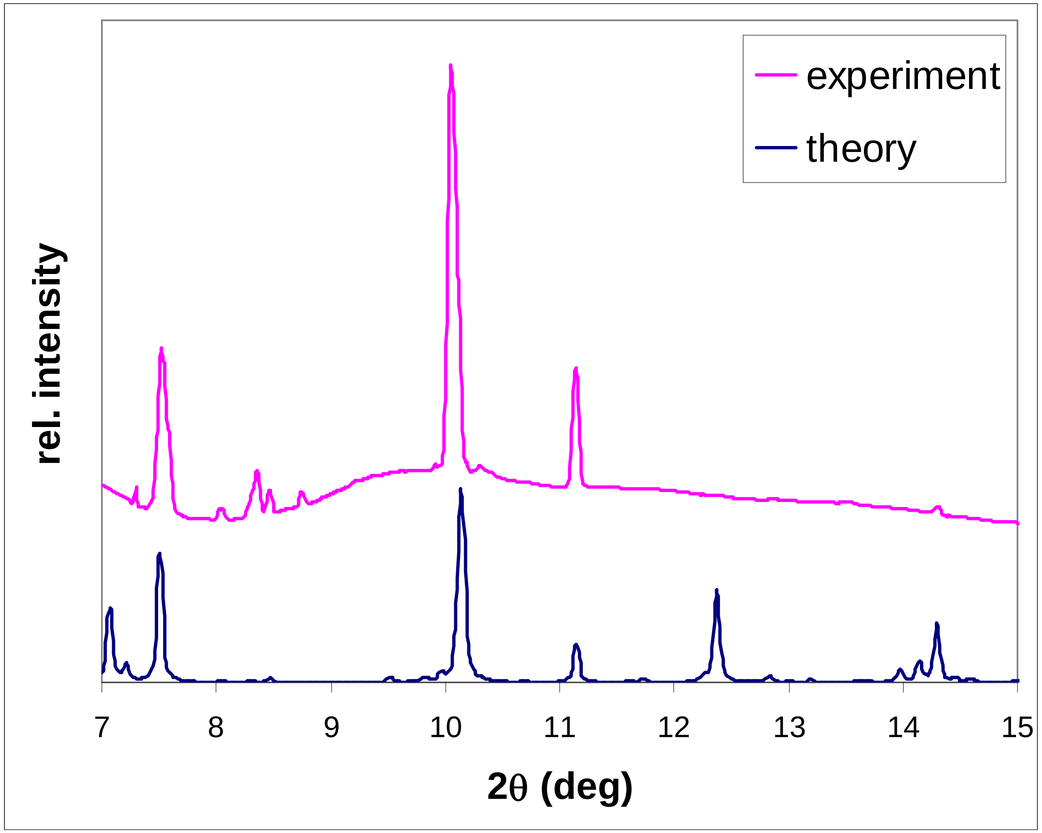
Theoretical structure determination

Step 4: Geometry optimization using density functional theory (DFT)

- Most accurate
- Validation of ReaxFF results
- Orthorhombic cell: $\alpha = \beta = \gamma = 90^o$
  - $V = 332$ Å^3 ($\rho = 479$ kg/m^3)
  - $a = 6.872$ Å
  - $b = 7.342$ Å
  - $c = 6.608$ Å



Comparison of XRD spectra



$\alpha = \beta = \gamma = 90^o$

V = 332 Å^3

a = 6.872 Å

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c = 6.608 Å

Pnnm space group (nr. 58)

- All experimental peaks match peaks for theoretically determined structure
- Intensities do not match due to coarse crystallinity of sample

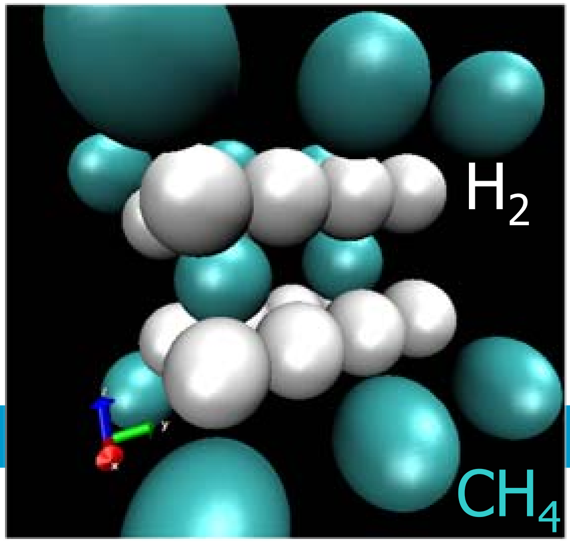
$CH_4(H_2)_4$ summary

Structure

- Orthorhombic methane substructure
- 2 distinct hydrogen sites

Approach is promising

- Theoretical calculations
- Experimental constraints

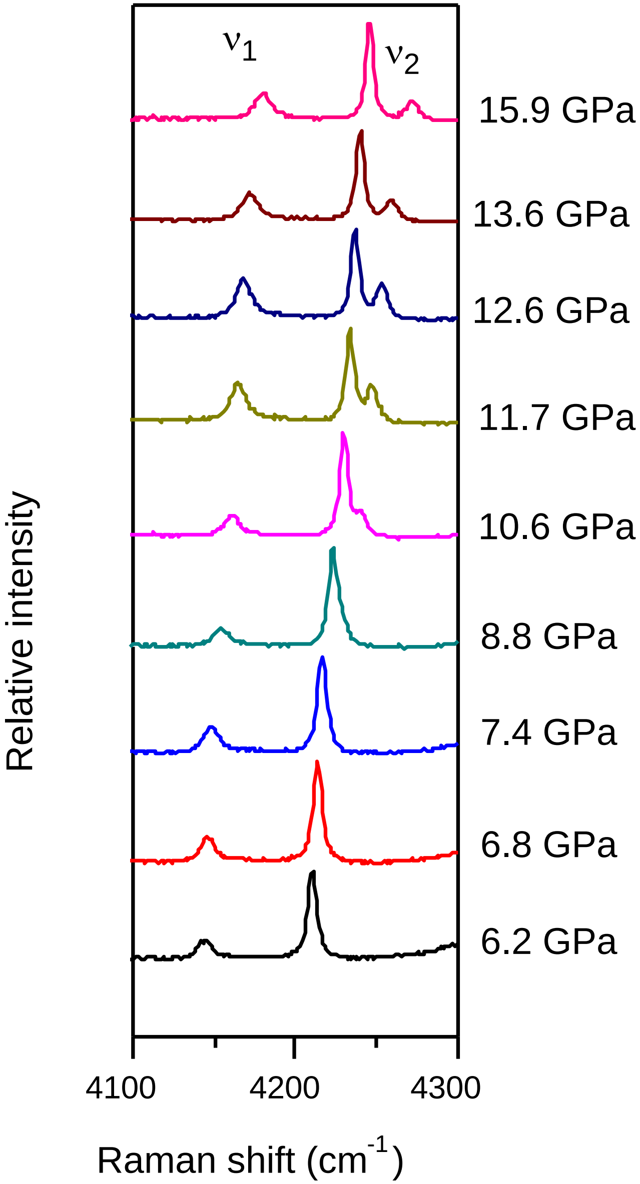


The next seven months and beyond

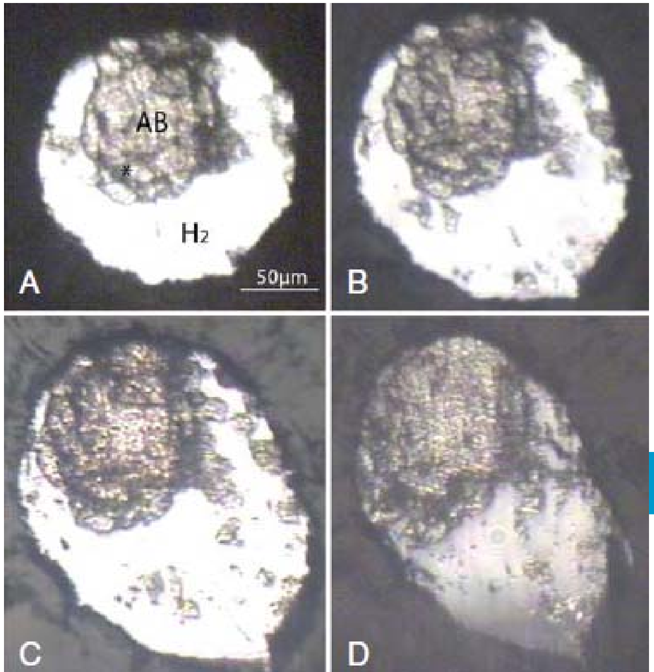
- Improve conditions for $CH_4(H_2)_4$
  - Add chemical stabilizers using calculations, test experimentally
  - Study with lower pressure, more precise apparatus
  - Study other CH_4+H_2 phases, e.g. $CH_4(H_2)_2$
- Repeat approach with other systems
  - e.g. NH_3+H_2, NH_3BH_3+H_2

Cailletet apparatus and the windowed autoclave

Ammonia Borane + H_2

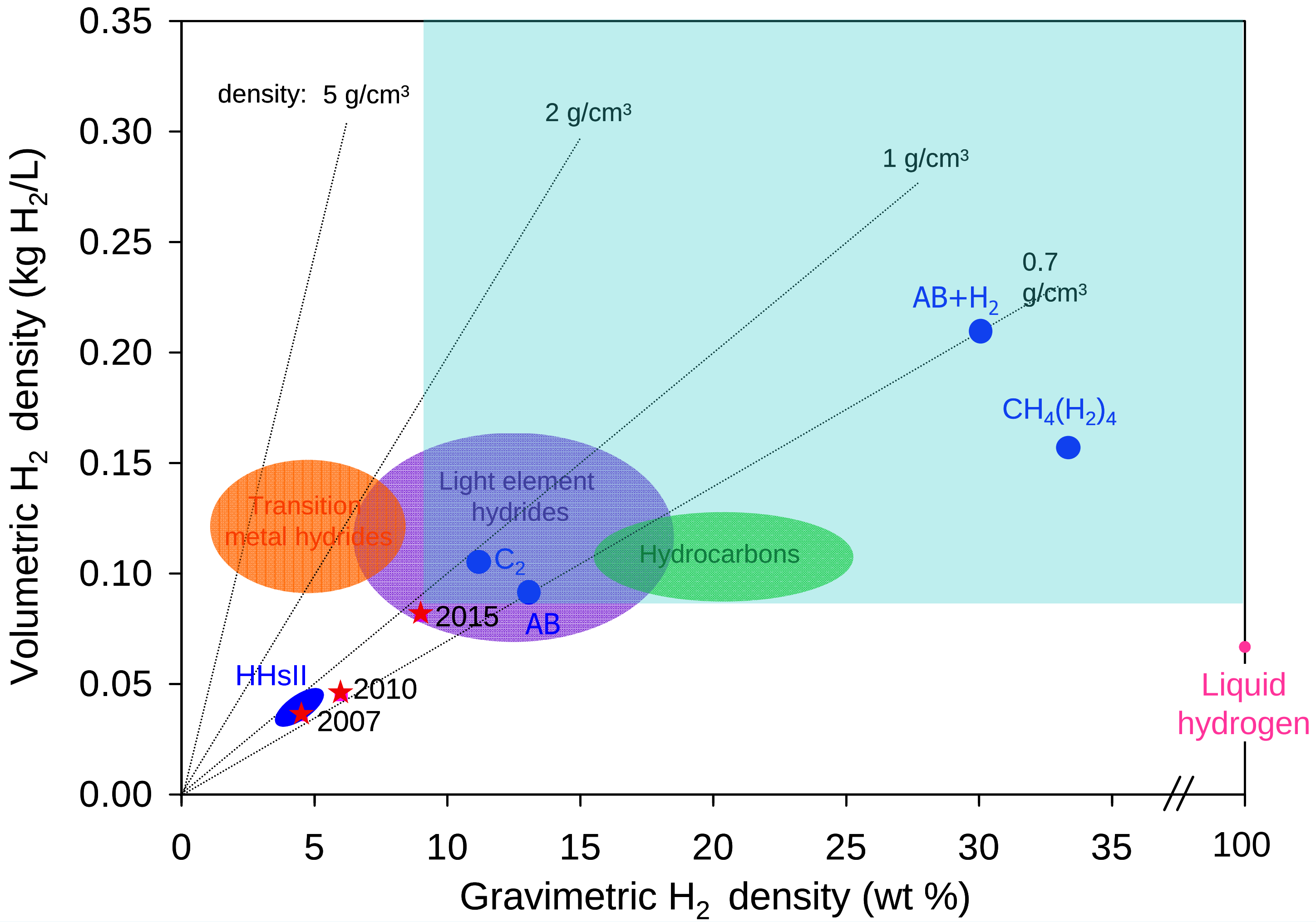


- $NH_3BH_3 \rightarrow NH_2BH_2 + H_2 \rightarrow NHBH + H_2$
- New phase in AB + H_2 system found at 6 GPa
- This AB–H_2 compound can store an estimated 8–12 wt % molecular H_2 in addition to the chemically bonded H_2 in AB
- What is the structure?
- Can we stabilize this compound?



Y. Lin *et al*, *PNAS* 2009

Hydrogen Storage Capacity



W. Mao *et al*, Physics Today 2007

Outlook

Discovery

- Very few hydrogen-rich systems have been explored at high pressure → potential for many novel structures and phases

Recovery & Practical Use

- These materials need to synthesized near ambient conditions → demonstrate that conditions can be improved, synthesis can be scaled up, study kinetics

Acknowledgements

Global Climate and Energy Project

Computer resources:

- Vanderbilt University

Experimental facilities:

- Extreme Environments Laboratory, Stanford University
- Geophysical Laboratory, Carnegie Institution of Washington
- Advanced Photon Source, Argonne National Laboratory