High capacity molecular hydrogen storage in novel crystalline solids

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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 $\rightarrow$ 5.5 GPa, 55,000 bar
  - High temperature $\rightarrow$ $>1500^\circ$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: $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$
- Tetrahedral bonding of carbon in methane mimics diamond

Diamond Growing in a Plasma Reactor

Element 6
Example: H$_2$+H$_2$O system

- H$_2$ clathrate, H$_2$(H$_2$O)$_2$, 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

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 + H₂ clathrate at 277.3 K at ambient pressure
- H₂ 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

- **Liquid hydrogen** density: 5 g/cm³
- **2 g/cm³**
- **1 g/cm³**
- **0.7 g/cm³**

**Diagram:**
- **Gravimetric H₂ density (wt %) vs. Volumetric H₂ density (kg H₂/L)**

**Areas:**
- **Transition metal hydrides**
- **Light element hydrides**
- **Hydrocarbons**

**Markings:**
- **HHsII**
- **C₂**
- **2010, 2015**
- **Liquid hydrogen**

**Source:**
W. Mao et al, Physics Today 2007
CH$_4$ + H$_2$ system

M. S. Somayazulu et al., Science 1996
\( \text{CH}_4(\text{H}_2)_4 \)

Raman spectroscopy:

Hydrogen vibron region

\( \text{CH}_4(\text{H}_2)_4 (s) \)

\( \text{CH}_4 + 4 \text{H}_2 (l) \)

2 hydrogen sites?

Melting curve:

W. Mao et al, CPL 2005
$\text{CH}_4(\text{H}_2)_4$

- 33.4 wt% molecular hydrogen
- 50.2 wt% total hydrogen
- Stable at high pressures or low temperature
- Unknown structure
Structure determination of \( \text{CH}_4(\text{H}_2)_4 \)

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

→ Insight into \( \text{H}_2 \) interactions with host materials
→ Design of optimized hydrogen storage material
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$^3$
CH$_4$(H$_2$)$_4$ diffraction

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

$T = 200 \text{ K, } p = 3.5 \text{ GPa}$

$(\lambda = 0.40747 \text{ Å})$
Theoretical structure determination

Step 1: Generation of Multiple Initial Configurations:
→ Generation of $1.1 \times 10^{11}$ Random Triclinic (Unit) Cells
→ 1100 runs of $1 \times 10^8$ configurations each

- Fixed $T$, $\rho$, $N_i$
  (298 K, 5.8 GPa, 16 H$_2$ and 4 CH$_4$)
- Randomly selected $\rho$, $\alpha$, $\beta$, $\gamma$, $a$, $b$, $c$
  $0.75 \cdot \rho_{\text{expected}} < \rho < 1.25 \cdot \rho_{\text{expected}}$
  $55^\circ < \alpha, \beta, \gamma < 125^\circ$
  $0.5 < b/a, c/a < 1.5$
- 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 Å³)

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 ($V = 333 \, \text{Å}^3$)

Theoretical structure determination

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

- Most accurate
- Validation of ReaxFF results
- Orthorhombic cell: $\alpha = \beta = \gamma = 90^\circ$
  - $V = 332 \, \text{Å}^3$ ($\rho = 479 \, \text{kg/m}^3$)
  - $a = 6.872 \, \text{Å}$
  - $b = 7.342 \, \text{Å}$
  - $c = 6.608 \, \text{Å}$
Comparison of XRD spectra

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

\[ \alpha = \beta = \gamma = 90^\circ \]
\[ V = 332 \text{ Å}^3 \]
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Pnnm space group (nr. 58)
CH₄(H₂)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$_3$BH$_3$+H$_2$
Ammonia Borane + H₂

- NH₃BH₃ → NH₂BH₂ + H₂ → NHBH + H₂
- New phase in AB + H₂ system found at 6 GPa
- This AB–H₂ compound can store an estimated 8–12 wt % molecular H₂ in addition to the chemically bonded H₂ in AB
- What is the structure?
- Can we stabilize this compound?
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
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