



# Inorganic Clathrates for Hydrogen Storage

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# Overview

## Timeline

- Start 04/01/2005
- End 04/01/2009
- 20% complete

## Budget

- Total project funding
  - \$1,160,351 from DOE
  - \$290,088 from CIW
- Funding for FY05 : \$200,000 from DOE, \$50,000 from CIW
- Funding for FY06 : \$50,000 from DOE, \$12,500 from CIW

## Barriers

- Weight and Volume
- Refueling Time
- Hydrogen Capacity and Reversibility
- Lack of Understanding of Hydrogen Physiosorption

## Partners

- LANL LANSCE-12, Yusheng Zhao
- BNL, NSLS, Chi-Chang Kao
- PNNL, Thomas Autrey
- NIST, Dan Neuman, Terry Udovic, Craig Brown, and Juscelino Leao



# Objectives

Develop and demonstrate reversible hydrogen storage **inorganic clathrate** materials with at least 7 wt.% gravimetric and 50 g H<sub>2</sub>/L materials-based volumetric capacity, allowing refueling time 1kg H<sub>2</sub>/min, with potential to meet DOE 2010 system-level targets.

- H<sub>2</sub>-CH<sub>4</sub>-X and H<sub>2</sub>-H<sub>2</sub>O-X Systems, novel inorganic clathrates. Explore P-T conditions and additional components X (promoters, or guest molecules ) that will stabilize the clathrate structure.
- Computer simulation study of binary and ternary systems to understand structural details and stability, molecular dynamics to predict new phases with a potential for hydrogen storage
- A dedicated gas loading system and large volume cells has to be developed for synthesis and recovery of hydrogen-based molecular compounds. The cells and gas loading system will be used at neutron facilities in structural and vibrational dynamics studies, for investigation and optimization of new low-pressure synthesis routes and discharge kinetics.



# Approach

- Explore P-T conditions and additional components X (promoters, or guest molecules ) that will stabilize the clathrate structure. Look for novel inorganic clathrate structures with larger cages capable to entrap hydrogen.
- Computer simulation study of binary and ternary systems to understand structural details and stability, molecular dynamics to predict new phases and characterize their stability formation kinetics
- A dedicated gas loading system and large volume cells are being developed for synthesis and recovery of hydrogen-based molecular compounds. The gas cells are used at neutron facilities in structural and vibrational dynamics studies, and will be adapted for investigation and optimization of new low-pressure synthesis routes and discharge kinetics.



# Technical Approach

- $\text{H}_2\text{-H}_2\text{O}$  system
- $\text{H}_2\text{-H}_2\text{O-X}$  systems, select X from different materials categories that form clathrates ( $\text{H}_2\text{O-X}$ )
  - ☐ Argon (very small, double occupation, space for  $\text{H}_2$ )
  - ☐ Organic molecules e.g. trimethylamine  $4(\text{CH}_3)_3\text{N-41H}_2\text{O}$ 
    - (guest location fixed, nitrogen distort the cage structure slightly)
  - ☐ Strong acid e.g.  $\text{HBF}_6$  or  $\text{HClO}_4$  (anionic guest)
  - ☐ Tetrahydrofuran (THF)
  - ☐ Strong cages, i. e.  $(\text{LiOH})_x(\text{H}_2\text{O})_{1-x}$
- $\text{H}_2\text{-X-CH}_4$  system, X is selected to optimize clathrate structure, X could be a mixture of water and all of the above
- $\text{H}_2\text{-AB}$  ammonia borane ( $\text{NH}_3\text{BH}_3$ ) clathrate, dual  $\text{H}_2$  storage

**Goal: Stabilize clathrate at near ambient T and P**

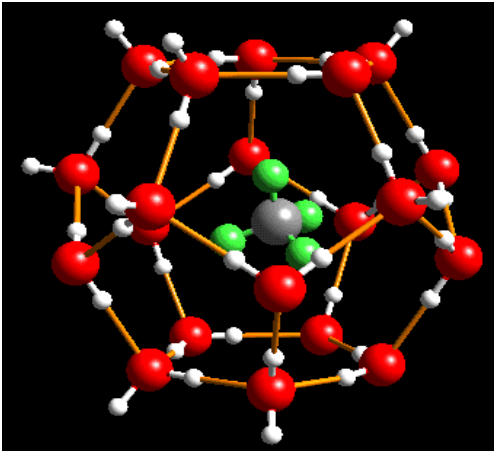
**Maximize  $\text{H}_2$  capacity**



# Theoretical Descriptions Relies on a Three-Prong Approach

Computational methods order with increasing accuracy:

1. Classical simulation: molecular dynamics with 1000s of atoms
2. Ab initio level description: structure relaxations in unit cell
3. Quantum Monte Carlo calculation: static calculations



- Molecular dynamics using predefined force-fields:

$$F = m a$$

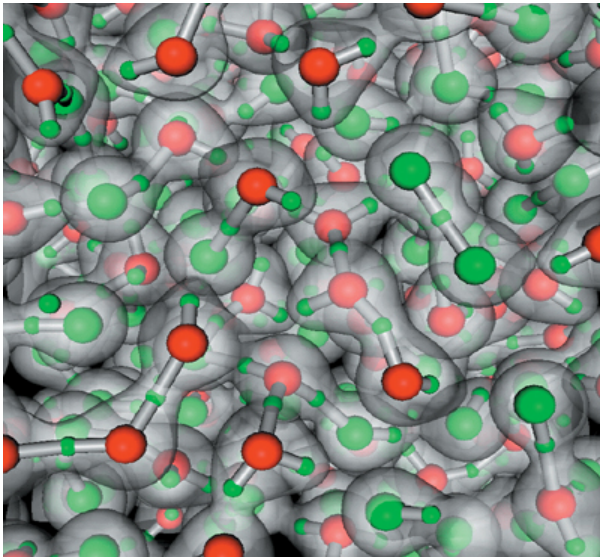
- Very fast** → Simulations of many cages possible
- However, the accuracy depends on force fields that contain all information about chemical bonds and interactions.
- Study the cage stability with increasing T → **melting**.
- Combine results with free energy calculations.
- Introduce different guest molecules
- Use simulation to select promising guest candidates



# Theoretical Descriptions Relies on a Three-Prong Approach

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Ab initio simulation (Gygi, Livermore)

- Electrons are quantum mechanical (wavefunctions  $\Psi$ ).
- Schroedinger equation solved (density function theory)

$$\hat{H} \Psi = E \Psi$$

- Ions are classical:  $F = m a$
- Accurate host-guest interaction → cage deformation
- Disorder
- Electronic and vibrational properties
- Orientation of guest molecules e.g. off-center location
- High pressure properties

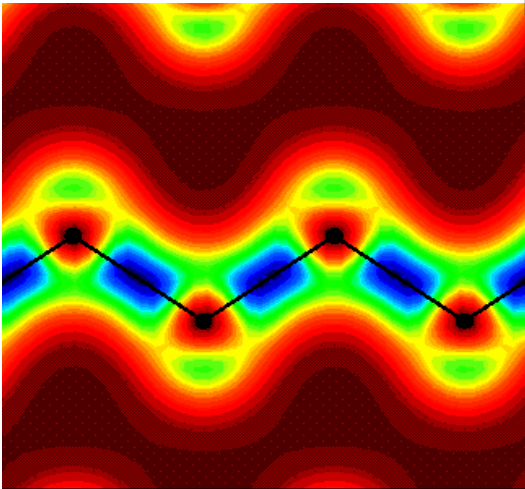


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In quantum Monte Carlo, one propagates a correlated ensemble of walkers in order to project out the groundstate wavefunction.



QMC study of exchange-correlation effects in bulk silicon (Foulkes).

## Advantages:

- Electronic correlation effects are included.
- Van der Waal interactions can be described.
- Study of  $\text{H}_2$  - water cage interaction
- Study of precise arrangements of molecules in cage
- Study of multiple  $\text{H}_2$  occupancy effects

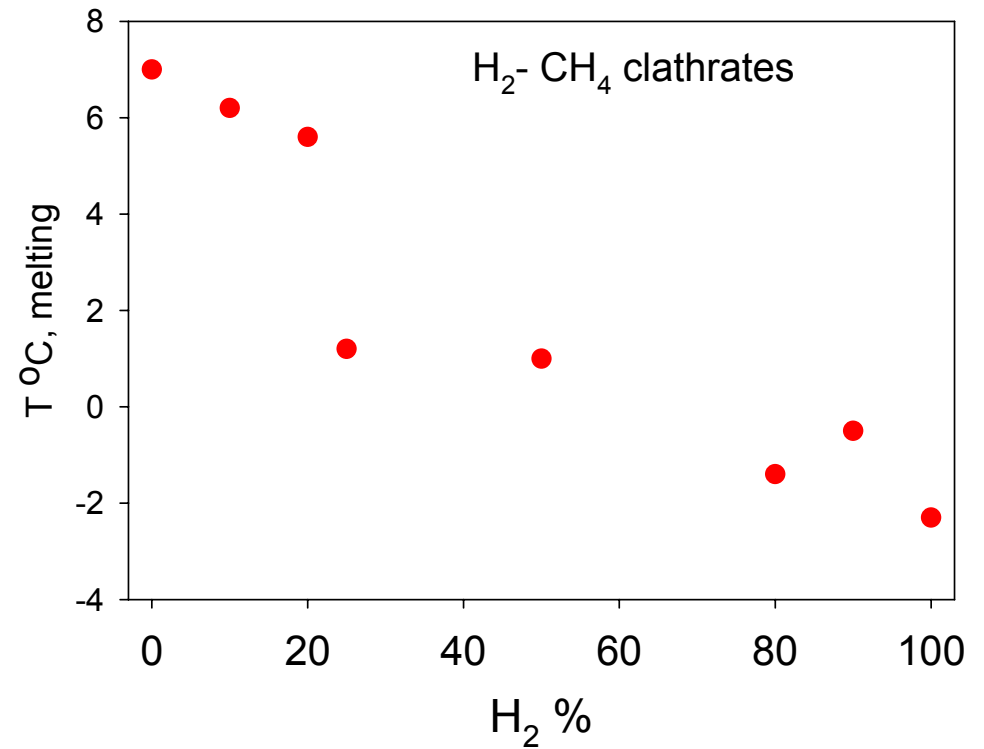
## Disadvantages:

- Method is very expensive
- Dynamics is currently not feasible





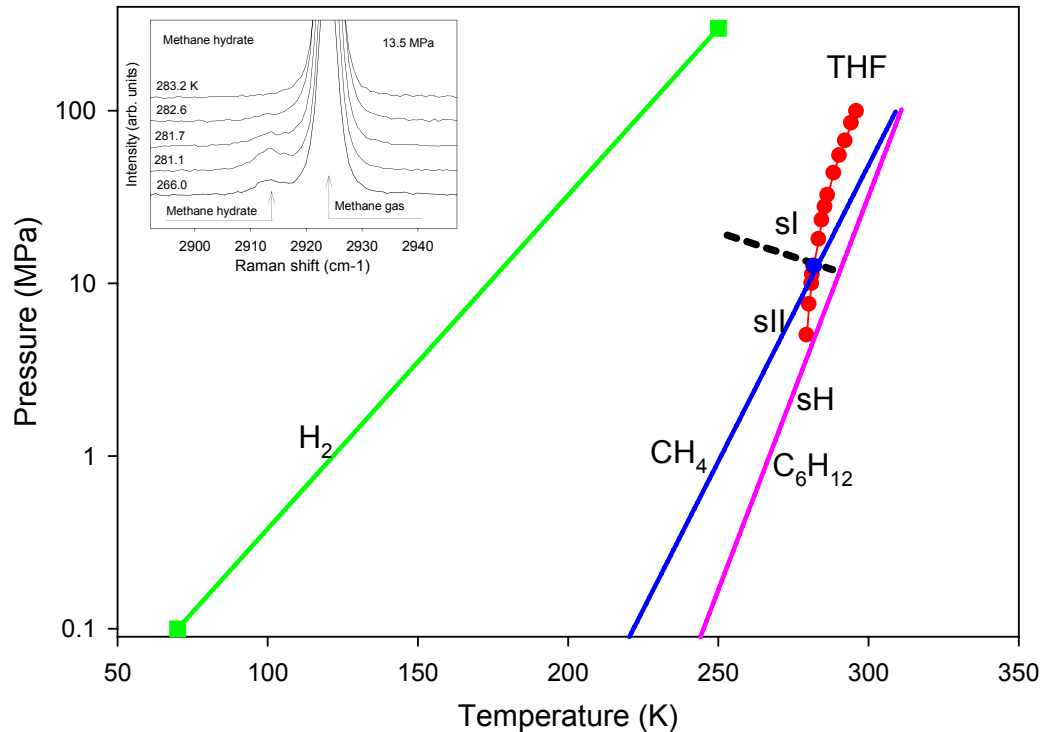
# Accomplishments



Modified diamond anvil press has been adapted for moderate pressure Raman (IR and XRD measurements also possible) The cylinder has a sapphire window, and the assembled cell can be clamped using screws. The piston assembly has a sapphire window and a copper spacer (sealed with teflon or indium rings) connected to a high pressure capillary.



# Accomplishments



Stability ranges of H<sub>2</sub>-(THF) – H<sub>2</sub>O , CH<sub>4</sub> – H<sub>2</sub>O clathrates.

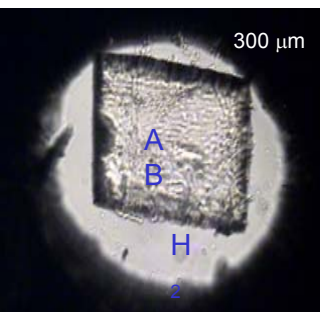
Inset: Raman spectra of methane clathrate measured in our Raman cell from a flake of methane hydrate ice.

Blue line – extrapolated stability line for CH<sub>4</sub>-H<sub>2</sub>O (sI & sII clathrates). Dashed line separates stability fields of sI and sII clathrates. Blue circle represents the methane clathrate decomposition measured in our Raman cell. Red circles – H<sub>2</sub>-THF-H<sub>2</sub>O clathrate (Florusse et al., Science 306, p.469, 2004); Green squares and line – stability line of H<sub>2</sub>-H<sub>2</sub>O sII clathrate (W. Mao et. al.). Magenta – extrapolated sH C<sub>6</sub>H<sub>12</sub>-H<sub>2</sub>O clathrate stability line.

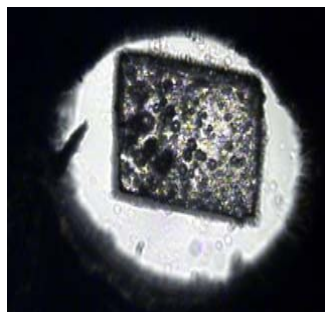


# Accomplishments *(with PNNL, T. Autrey)*

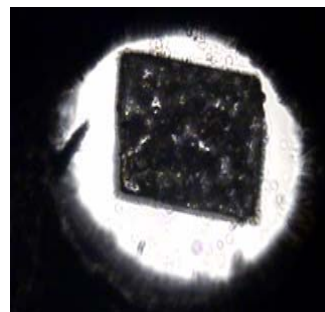
Increasing temperature series AB (ammonia borane  $\text{NH}_3\text{BH}_3$ )



Room  
temperature  
P = 7 kbars

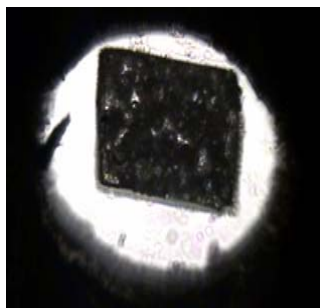


120°  
C

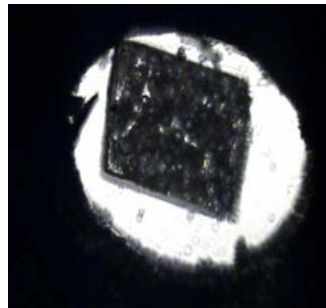


127°  
C  
melt

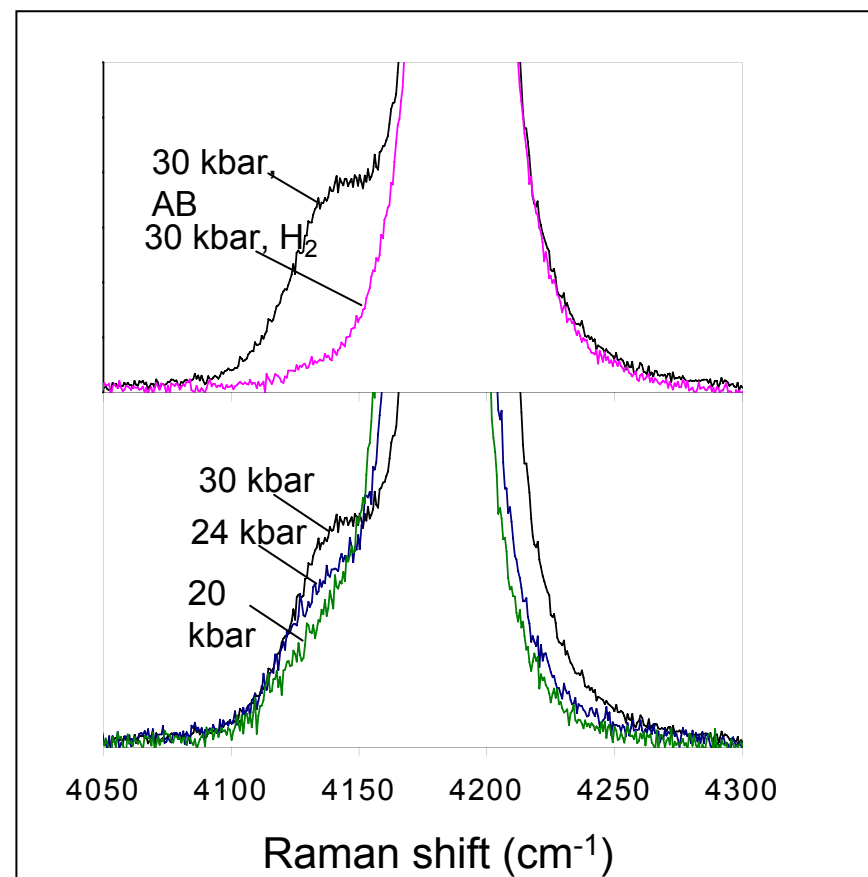
Increasing pressure series



Room  
temperature  
P = 10 kbars



Room  
temperature  
P = 30 kbars



Raman spectra of the hydrogen vibron region. Top figure shows comparison between  $\text{H}_2$  region and AB +  $\text{H}_2$  region. Small shoulder indicates  $\text{H}_2$  in the AB compound. Bottom figure shows AB region spectra at three different pressures. The estimate from Raman intensities for the incorporation of  $\text{H}_2$  into the AB structure is  $>3.3$  volume %.

**A possible application of this effect would be combined molecular and chemical storage in this compound, dual chemical and molecular storage (6%+3%=9% by volume)**



# *Accomplishments*

## Carnegie Panoramic Cells (with SNAP team)

- Panoramic cells.
  - With moissanite anvils these are capable of pressures to 30 GPa.
  - Sample volumes are quite small.
  - Right is a picture of Panoramic cell mounted on the VIVALDI beam line at ILL (sample is FeO single crystal).





# Accomplishments

Gas pressure cell designed to 7000 psi (~0.5 kbar).

- Water ( $D_2O$ ) and promoter molecules are added in powder crystal form to increase the surface area for the hydrogen gas absorption.
- Hydrogen is then added at ~1400 psi and the sample is heated to transition point of 270 K.
- After equilibration, the mixture is refrozen trapping hydrogen and allowing for the release of the excess hydrogen gas, so the pressure is now ambient.



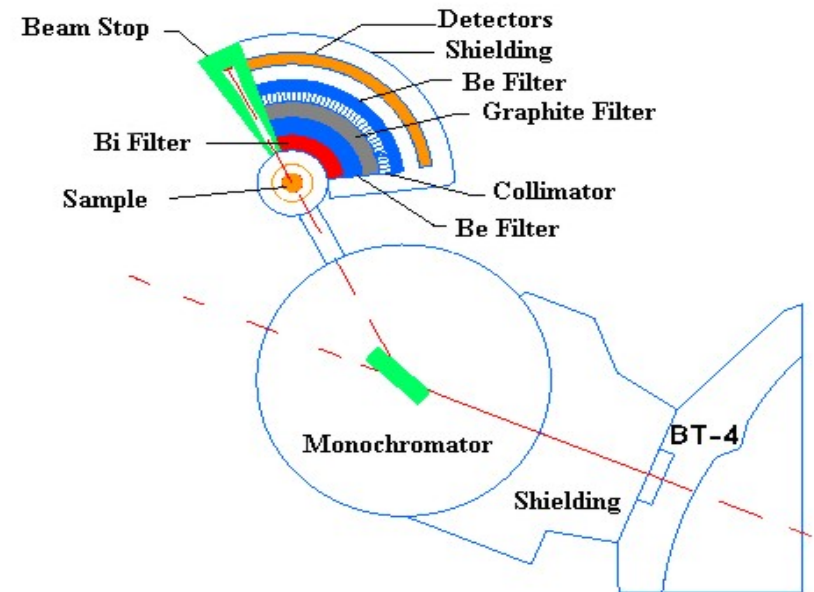
Cell design based on the work of Juscelino Leao, modified for slightly higher pressures



# Accomplishments

## FANS Instrument Setup (with NIST)

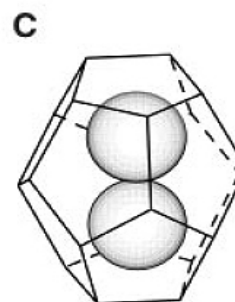
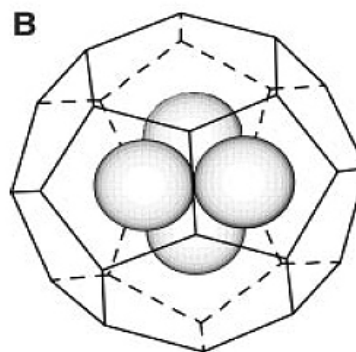
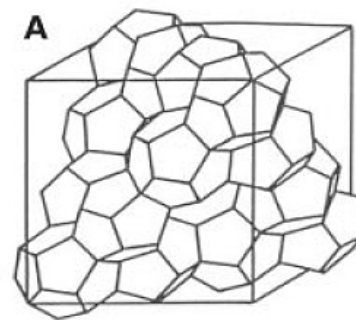
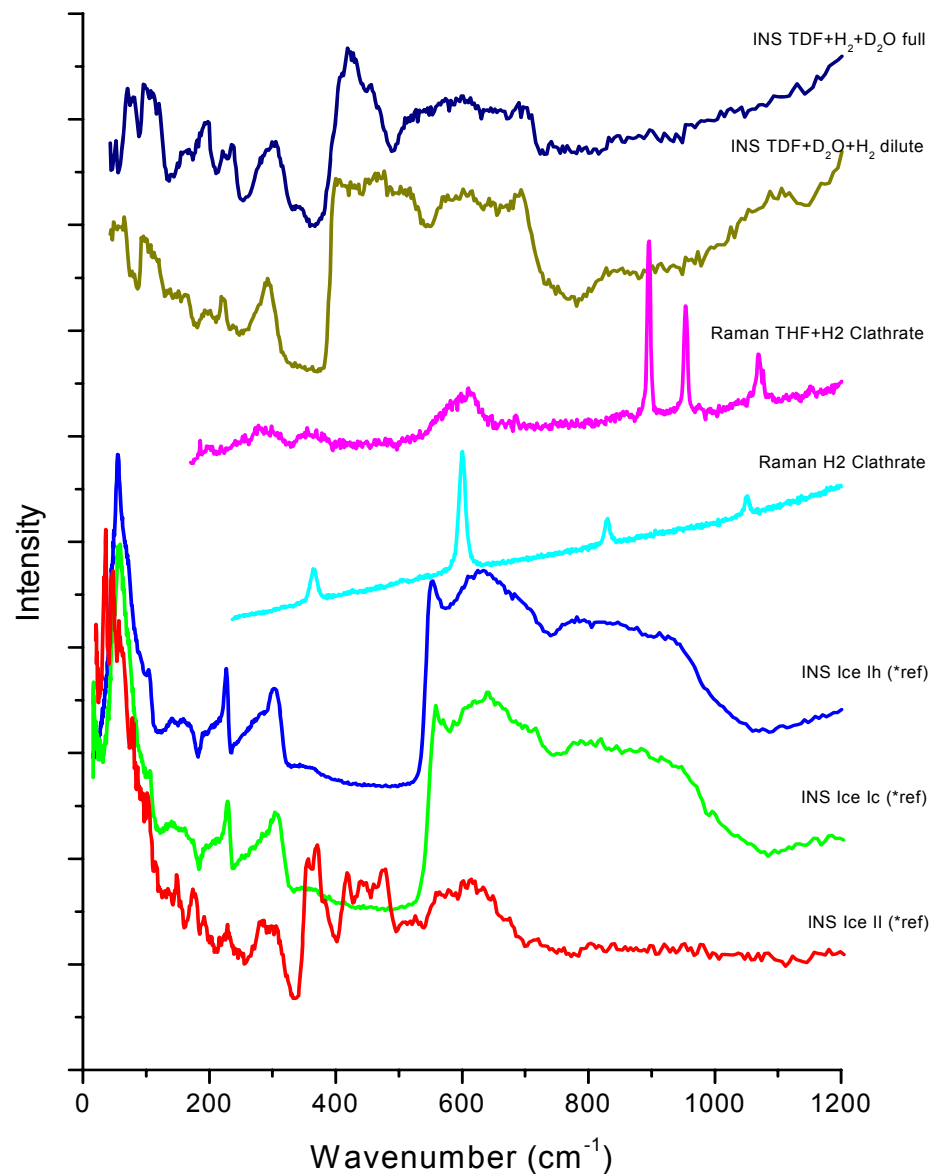
- Both the available Copper and Graphite monochromators were used to get a spectrum from 5 to 160 meV ( $40\text{--}1300\text{ cm}^{-1}$ ).
- Special thanks to Juscelino Leao for his help in the execution of these experiments







# Accomplishments

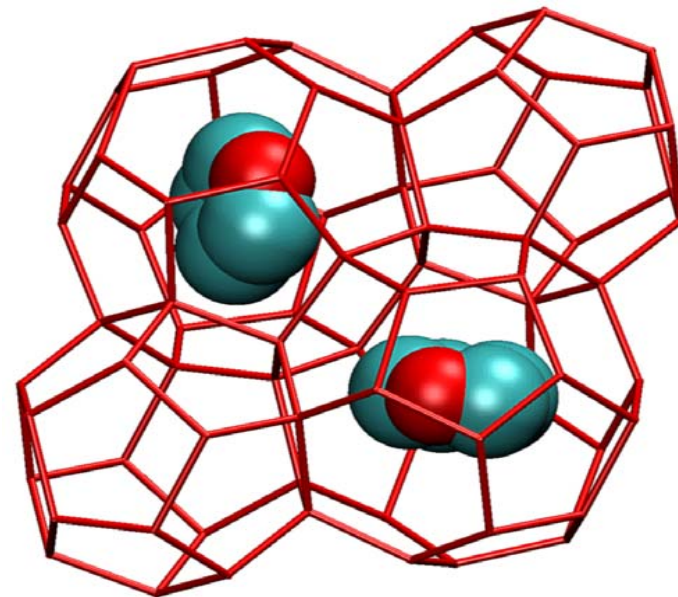
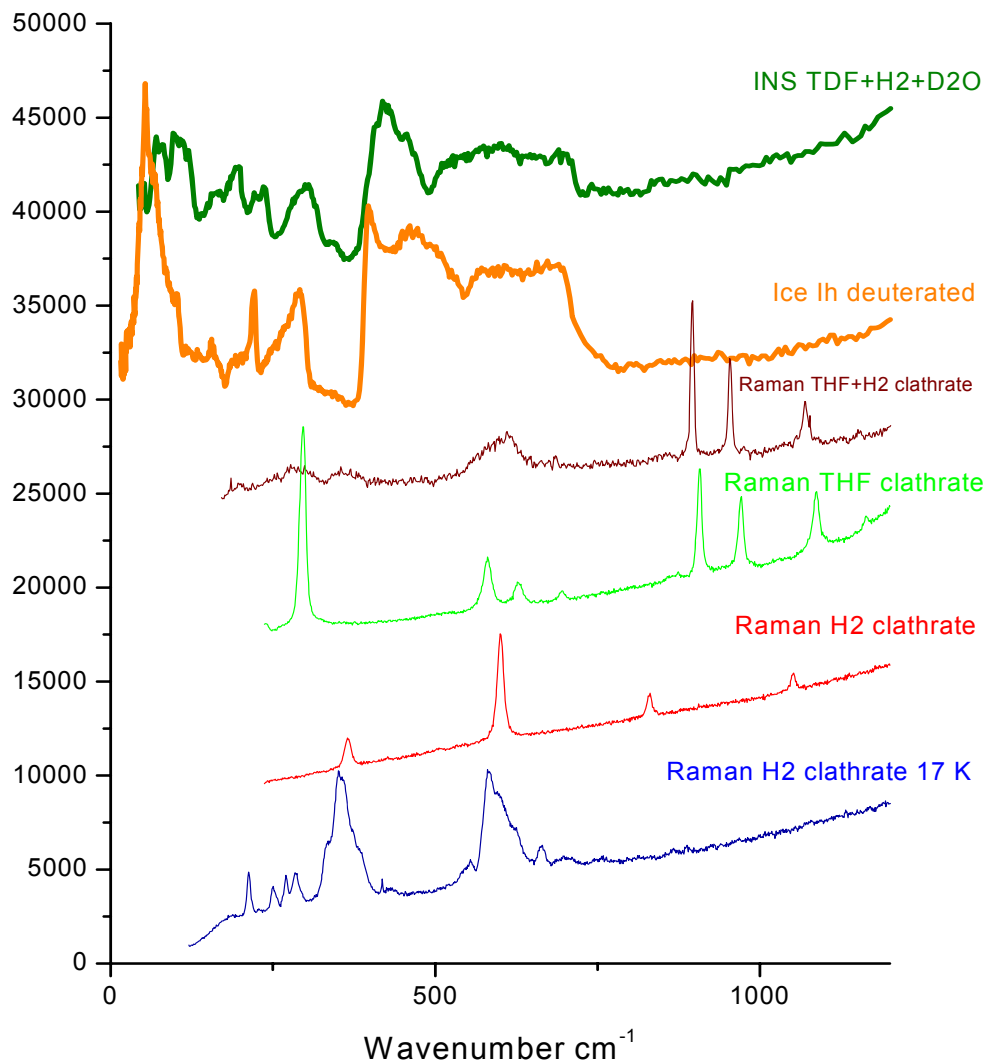


Clathrate hydrate compounds involving THF guest molecules were examined using Inelastic Neutron scattering at NIST (FANS).

INS on Ice from Jichen Li, J. Chem. Phys. (1996)



# Accomplishments

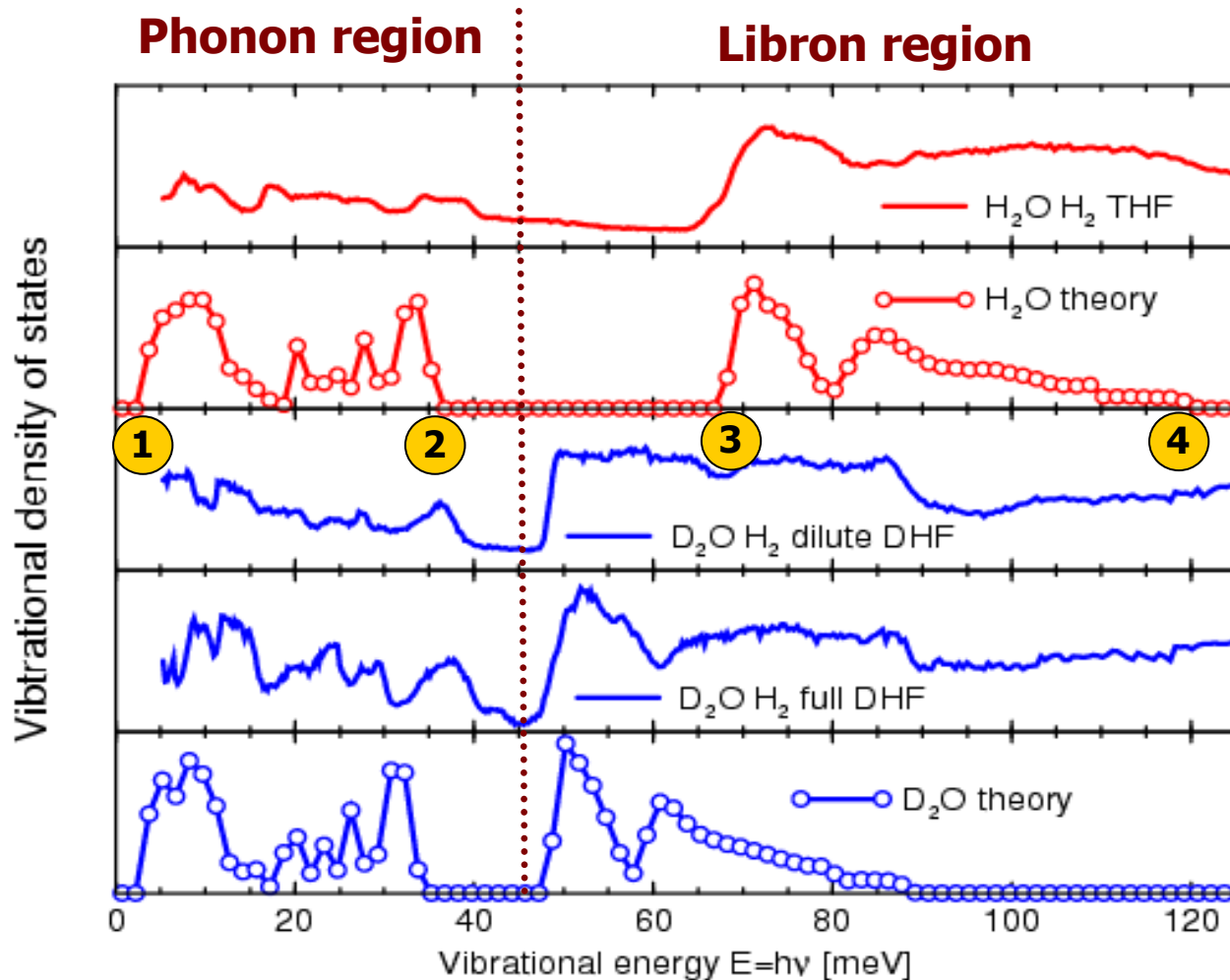


THF occupies the larger cages leaving the hydrogen free to occupy the smaller cages. Raman work was done to try and assign peaks empirically. Notice the differences between the hydrogen clathrate (green) and Ice (orange).





# Accomplishments

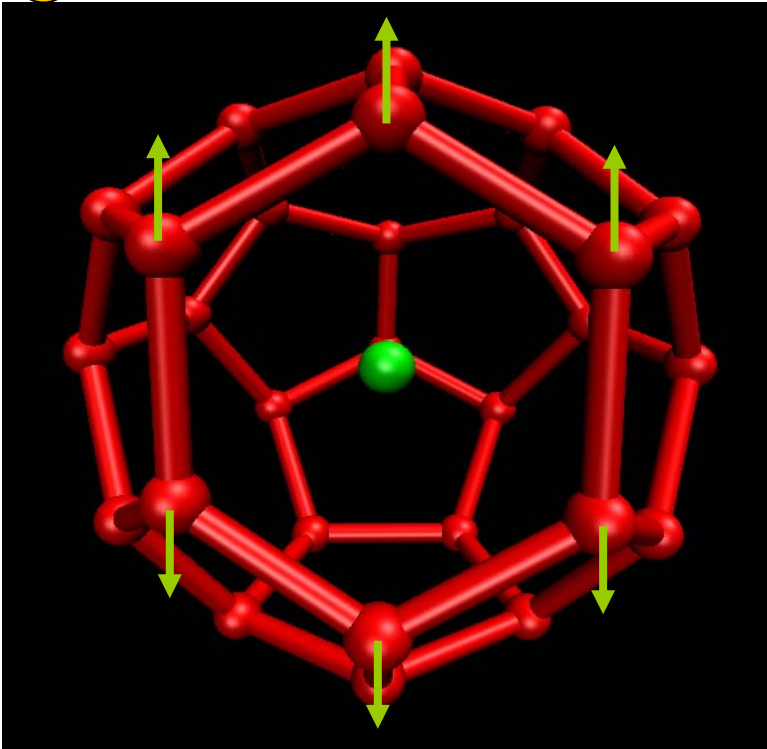


**Theory helps to interpret the vibrational spectra measured in neutron diffraction experiments at NIST**



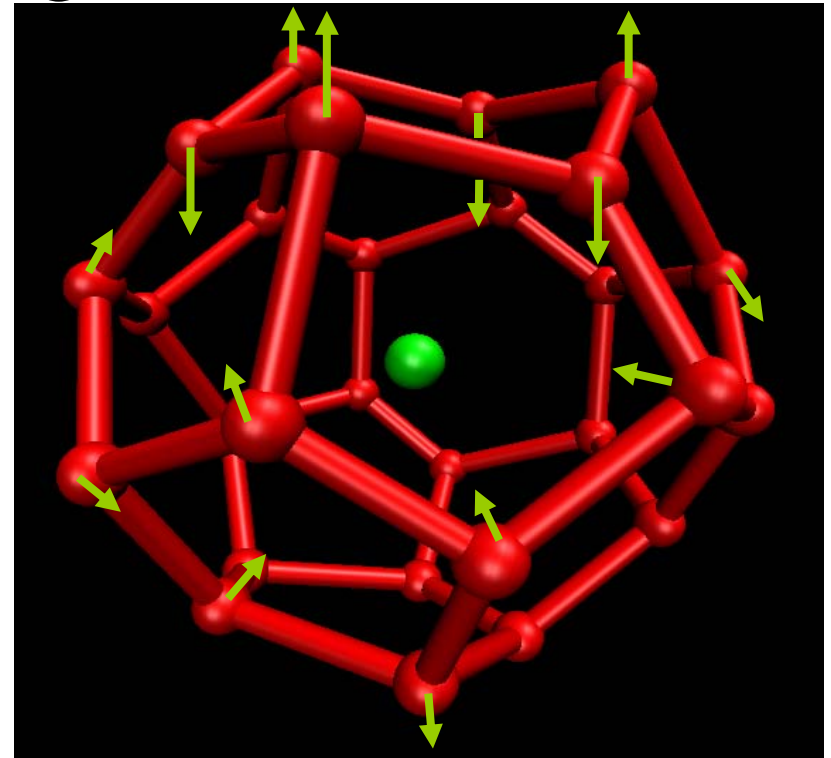
# The scattering of neutrons lead to different modes of cage vibration: **Phonons**

## 1 Low frequency phonon mode



Large cage **breathing motion**:  
The cage opens and closes like a clamp. The one **hexagon** facing out is **stretched**.

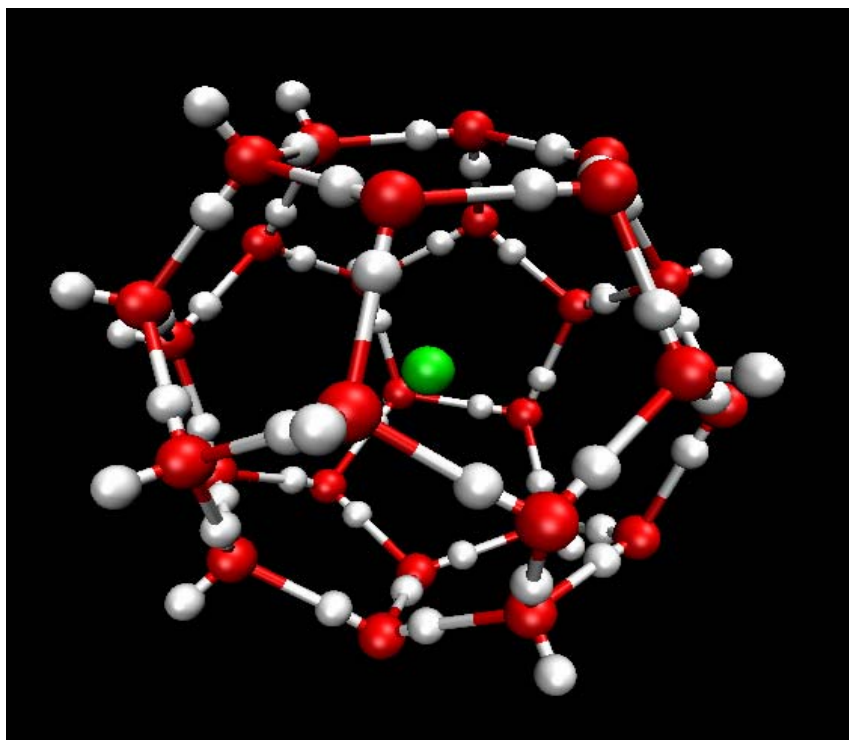
## 2 High frequency phonon mode



Large cage **surface distortion**:  
The **hexagon** on top is distorted like most other polygons



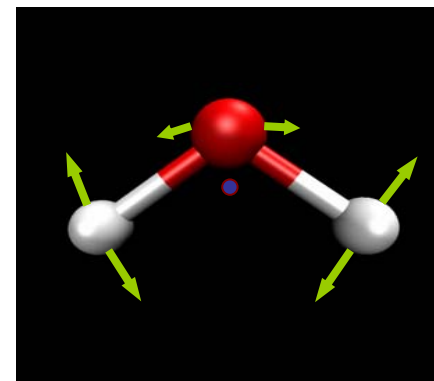
# The scattering of neutrons lead to different modes of cage vibration: **Librons**



The **libron** part of the vibrational spectrum is characterized by the **rotation of H<sub>2</sub>O molecules** around different axes.

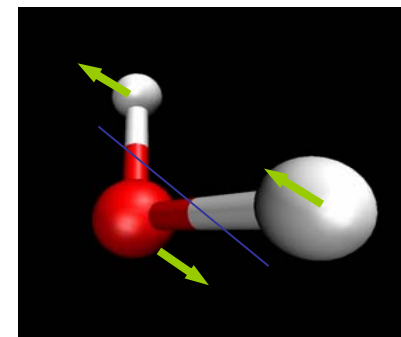
## 3 Low frequency libron mode

H<sub>2</sub>O molecules rotate primarily around an **axis perpendicular** to the molecular plane



## 4 High frequency libron mode

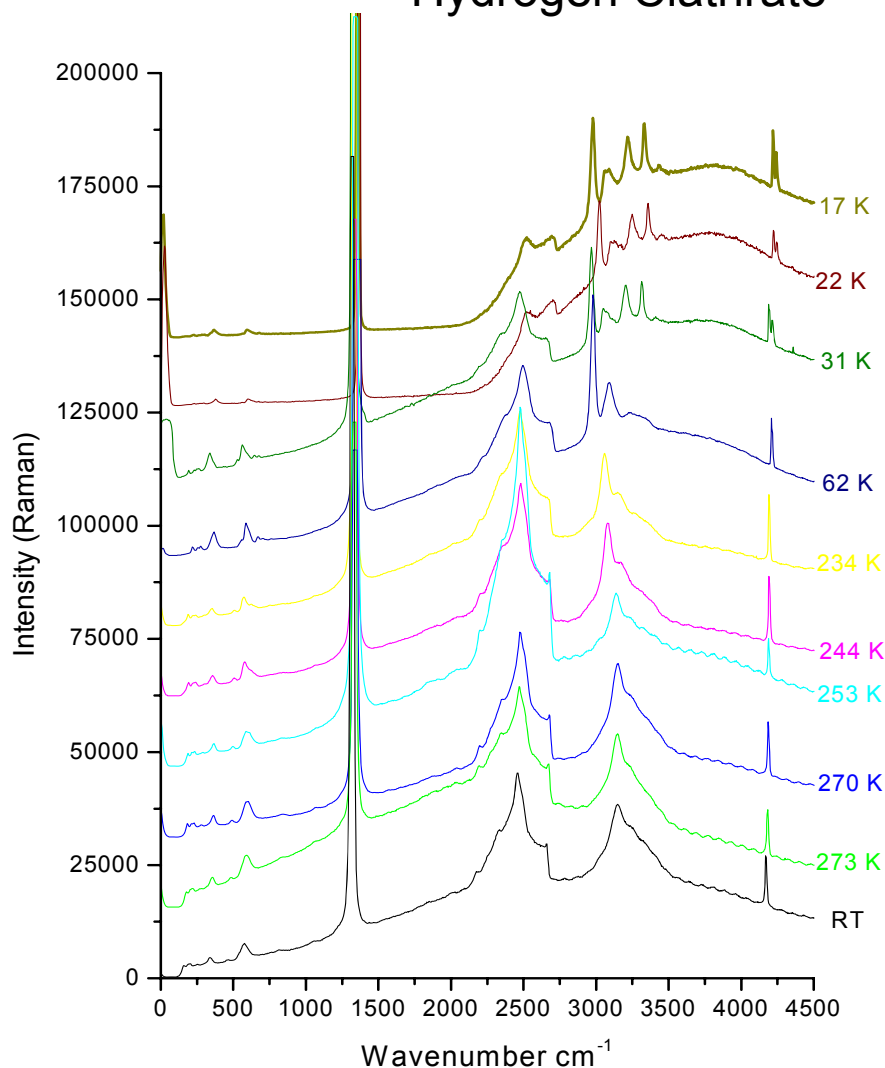
H<sub>2</sub>O molecules rotate primarily around an **axis parallel** to the line connecting H-H





# Accomplishments

## Hydrogen Clathrate



$\text{H}_2$  clathrate was examined as a function of temperature and pressure. Clathrate formation is exhibited by sharpening of O-H stretch ( $\sim 3100 \text{ cm}^{-1}$ ). Higher pressures ( $> 10 \text{ kbar}$ ) prohibited the formation of the hydrogen clathrate structure SII; the spectra shown most likely represent Clathrate C2 as discussed in Vos, et. al. Phys. Rev. Lett. (1993).

Low temperature vibrations are very unusual and may belong to a new clathrate form: further experiments are planned to elucidate the low-T clathrate structure and hydrogen intake.



# Future Work

## **Year 2006:**

Task 1: Further studies of  $\text{H}_2\text{-CH}_4\text{-X}$ ,  $\text{H}_2\text{-H}_2\text{O-X}$  systems, down-selection of two most promising compositions.

Task 2: Characterization of the optimized clathrate phases by Raman, IR, x-ray diffraction, and neutron diffraction.

Task 3: Investigation and optimization of new low-pressure synthesis routes and discharge kinetics.

Task 4: Computer simulation study of optimized ternary systems including molecular dynamics to predict new phases and characterize their stability and structural details.

Task 5: A dedicated gas loading system will be modified and extended to allow measurements of the kinetics/thermodynamics of release and storage and measurements of gravimetric and volumetric capacity of new materials.

## **Year 2007:**

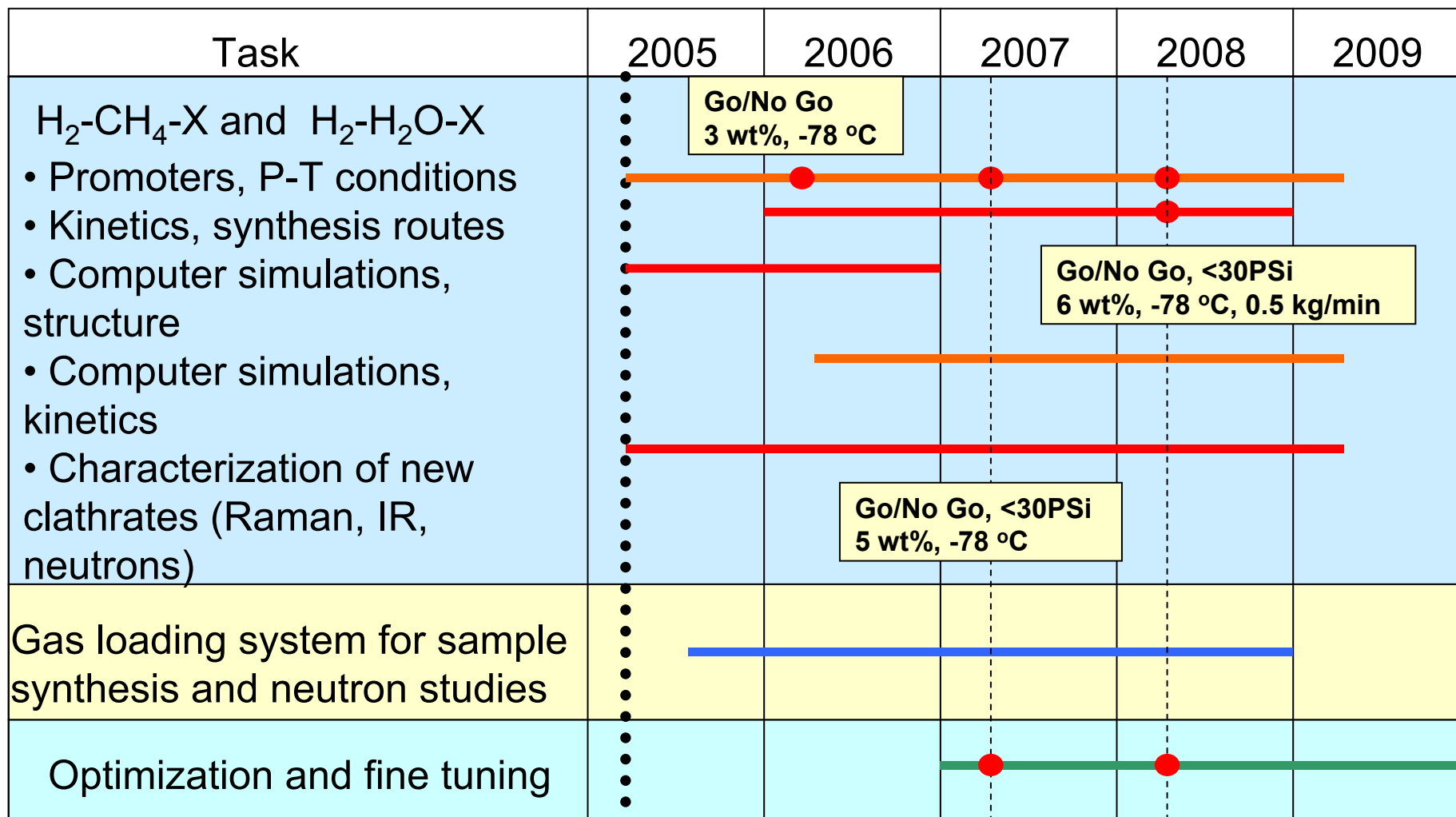
Task 6: Novel Clathrate Systems. Explore P-T conditions and additional components X (promoters ) that will stabilize the large-cage clathrate structure, with faster formation kinetics.

Task 7: Computer simulation study of binary and ternary systems to understand structural details, kinetics, and stability.

Task 8: A dedicated gas loading system will be used for synthesis and recovery of hydrogen-based molecular compounds, their optimization and fine-tuning, in larger volumes ( $1\text{ cm}^3$ ). The system will be used at neutron facilities in structural and vibrational dynamics studies.



# Project Timeline





# *Publications and Presentations*

- H.-k. Mao, W. L. Mao, V. V. Struzhkin, Hydrogen Storage in Molecular Compounds, presented at ASM Int. Conf, Columbus, OH, October 18-21, 2004.
- W. L. Mao, V. V. Struzhkin, H.-k. Mao, and R. J. Hemley, P-T stability of the van der Waals compound  $(\text{H}_2)_4\text{CH}_4$ , Chem. Phys. Lett. 402, 66-70, 2005.
- K. Lokshin, Y. Zhao, D. He, W. L. Mao, H.-k. Mao, R. J. Hemley, M. V. Lobanov, and M. Greenblatt, Structure and dynamics of hydrogen molecules in the novel clathrate hydrate by high pressure neutron diffraction, Phys. Rev. Lett., 93, 125503, 2004.
- W. L. Mao and H.-k. Mao, Hydrogen storage in molecular compounds, PNAS 101, 708-710, 2004.
- W. L. Mao, "Hydrogen storage in molecular compounds," 2004 SSAAP Symposium, Albuquerque, NM, March 2004 (poster).
- W. L. Mao, "Hydrogen storage in molecular compounds," 2003 LANSCE User Group Meeting, Los Alamos Neutron Science Center, Los Alamos, NM, October 2003 (invited talk).
- W. L. Mao, "Neutron study of hydrogen clathrate," 2003 COMPRES Meeting, Santa Cruz, CA, June 2003 (poster).
- T. Jenkins, H.-k. Mao, W. Mao, B. Militzer, R. Hemley, V. Struzhkin "Hydrogen clathrate compounds for hydrogen storage by neutron and visible spectroscopy methods.", 230th ACS National Meeting, in Washington, DC, Aug 28-Sept 1, 2005 in Washington
- T. Jenkins, H.-k. Mao, W. Mao, B. Militzer, R. Hemley, V. Struzhkin " Spallation Neutrons and Pressure (SNAP): a state of the art high pressure diffractometer.", 230th ACS National Meeting, in Washington, DC, Aug 28-Sept 1, 2005 in Washington
- T. Jenkins, H.-k. Mao, W. Mao, B. Militzer, R. Hemley, V. Struzhkin "Hydrogen storage using clathrate hydrates examined by neutron scattering", Hydrogen-Metal Systems Gordon Research conference, July 10-15, 2005, Colby College, Waterville, ME
- W.L. Mao, "Hydrogen Storage in Molecular Compounds", Hydrogen-Metal Systems Gordon Research conference, July 10-15, 2005, Colby College, Waterville, ME
- H.-k. Mao, W. Mao, "Hydrogen Storage in Molecular Compounds", Wilhelm und Else Heraeus-Seminar on Hydrogen Storage with Novel Nanomaterials, 23 - 27 October 2005, Bad Honnef, Germany
- H. K. Mao, "Hydrogen storage in molecular compounds," H-workshop, Bad Honnef, Germany, October 2005 (invited talk).
- W. L. Mao, "Hydrogen storage in molecular compounds," IUCr 2005 Meeting, Florence, Italy, August 2005 (invited talk).