Structural study of clathrate hydrates by *in-situ* high-pressure neutron diffraction

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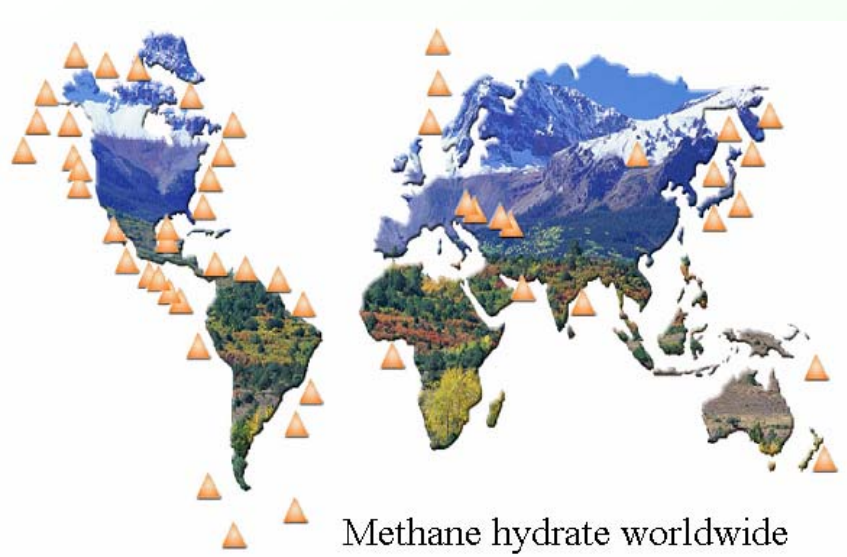
Outline

1. Clathrate hydrates of natural gases
2. Advanced setup for high-pressure low-temperature neutron diffraction
3. Hydrogen clathrate
   - Variation of occupancy and distribution of guest H_2 molecules
   - H_2 – H_2O phase diagram
   - Kinetics of hydrogen clathrate formation
4. Conclusions
5. Future plans

Clathrate hydrates of natural gases



Occurrence

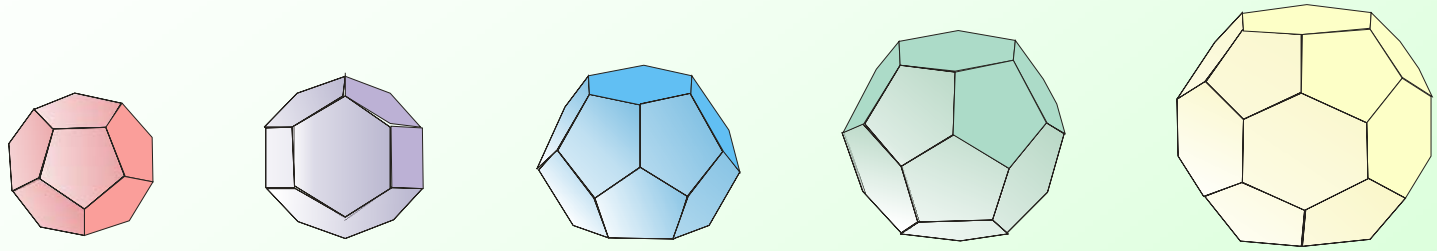
- Sea sediments (hydrocarbons, H_2S, CO_2)
- Gas\oil pipelines (hydrocarbons)
- Permafrost (CH_4, N_2, O_2)
- Polar ices (N_2, O_2)
- Planetary nebulae (CH_4, H_2, N_2, O_2)

Importance

- Future energy sources (CH_4, H_2- clathrates)
- Carbon sequestration (CO_2 - clathrate)
- Gas storage and separation
- Structures and stability → Multiple cage occupancy

Multiple cage occupancy in clathrate hydrates

Size discrepancy: H_2 (3.8Å), Ne (3.2Å), Ar (3.9Å), N_2 (4.6Å)



5^{12}	$4^3 5^6 6^3$	$5^{12} 6^2$	$5^{12} 6^4$	$5^{12} 6^8$
d ~ 7.7Å	d ~ 8.1Å	d ~ 8.6Å	d ~ 9.3Å	d ~ 11.4Å

Theoretical calculations:

Klaveren, E.P. et al. *J. Chem. Phys.* **114** (2001) 5745

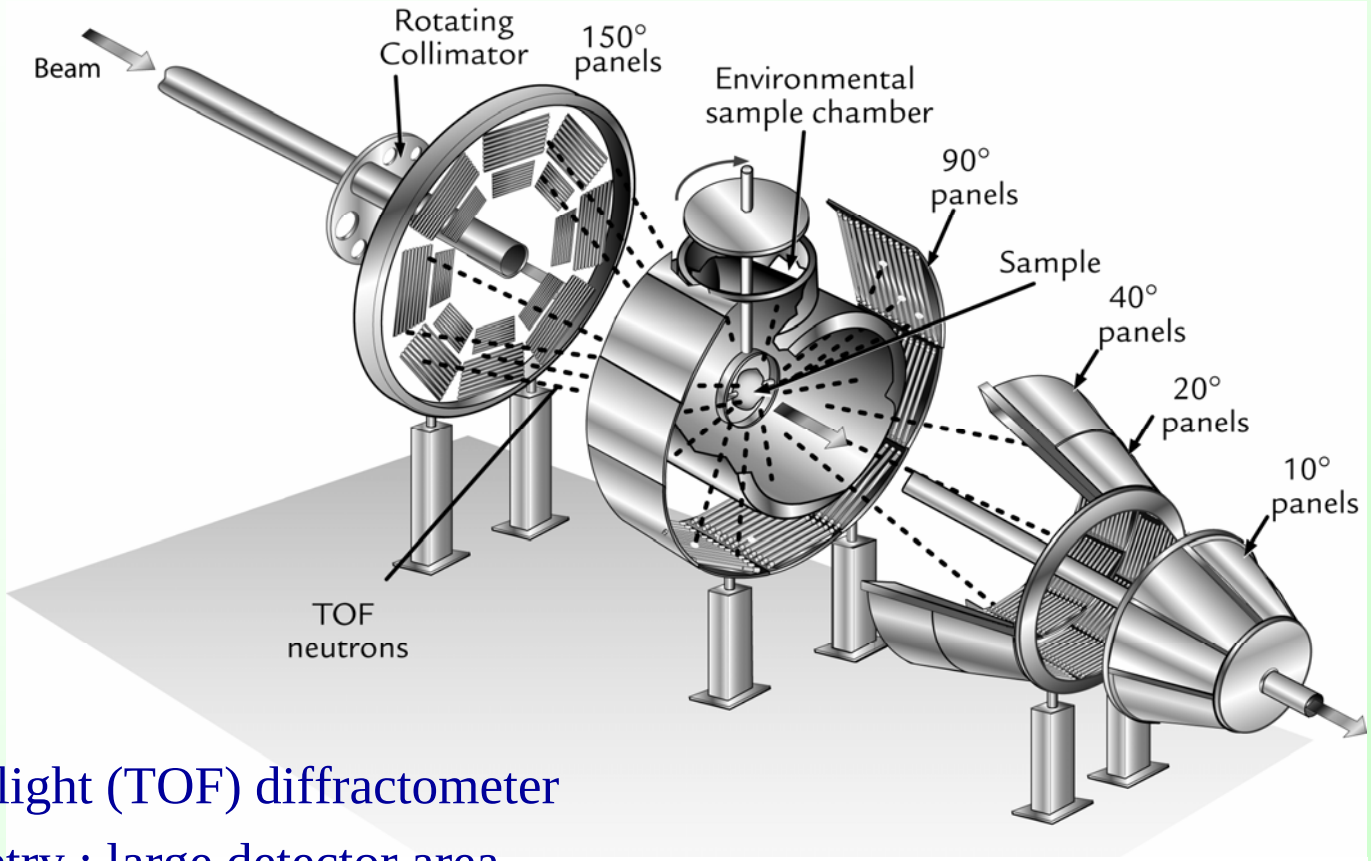
Patchkovskii, S., Tse, J.S. *Proc. Nat. Acad. Sci.* **100** (2003) 14645

Neutron diffraction:

Kuhs, W.F. et al. *J. Inclusion Phenom. Mol. Recognit. Chem.* **29** (1997) 65

Chazallon, B., Kuhs, W.F. *J. Chem. Phys.* **117** (2002) 308

High Pressure Preferred Orientation Neutron Diffraction



Time-of-flight (TOF) diffractometer

3D geometry : large detector area

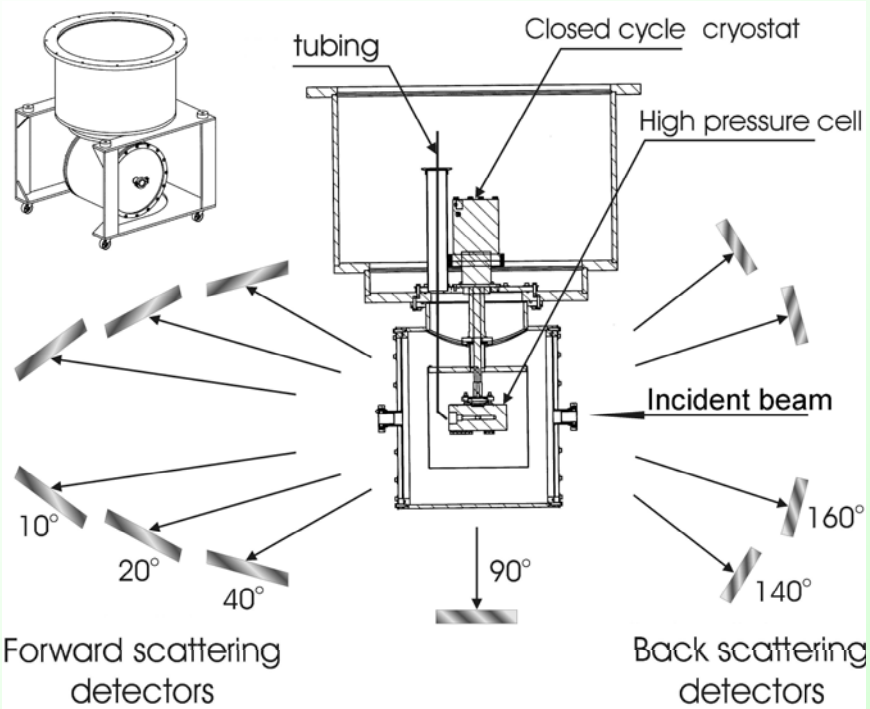
Very high neutron flux (~$2.7*10^7$ neutrons $cm^{-2}s^{-1}$)

Resolution: $\Delta d/d$ ~ 0.01 (90°), ~0.005 (150°)

Advanced Setup for High-Pressure and Low-Temperature Neutron Diffraction

Uniqueness of setup:

- No impurity scattering from the environment at 30-150˚ scattering angle
- Large sample volume and high intensity of HIPPO diffractometer



p ~ 1 – 10 kbar
T ~ 10 – 300 K

Applications:

- Rietveld and PDF structure analysis
- EOS, phase transformations
- Time-resolved studies (time step ~ 1 min, the shortest known data collection time)

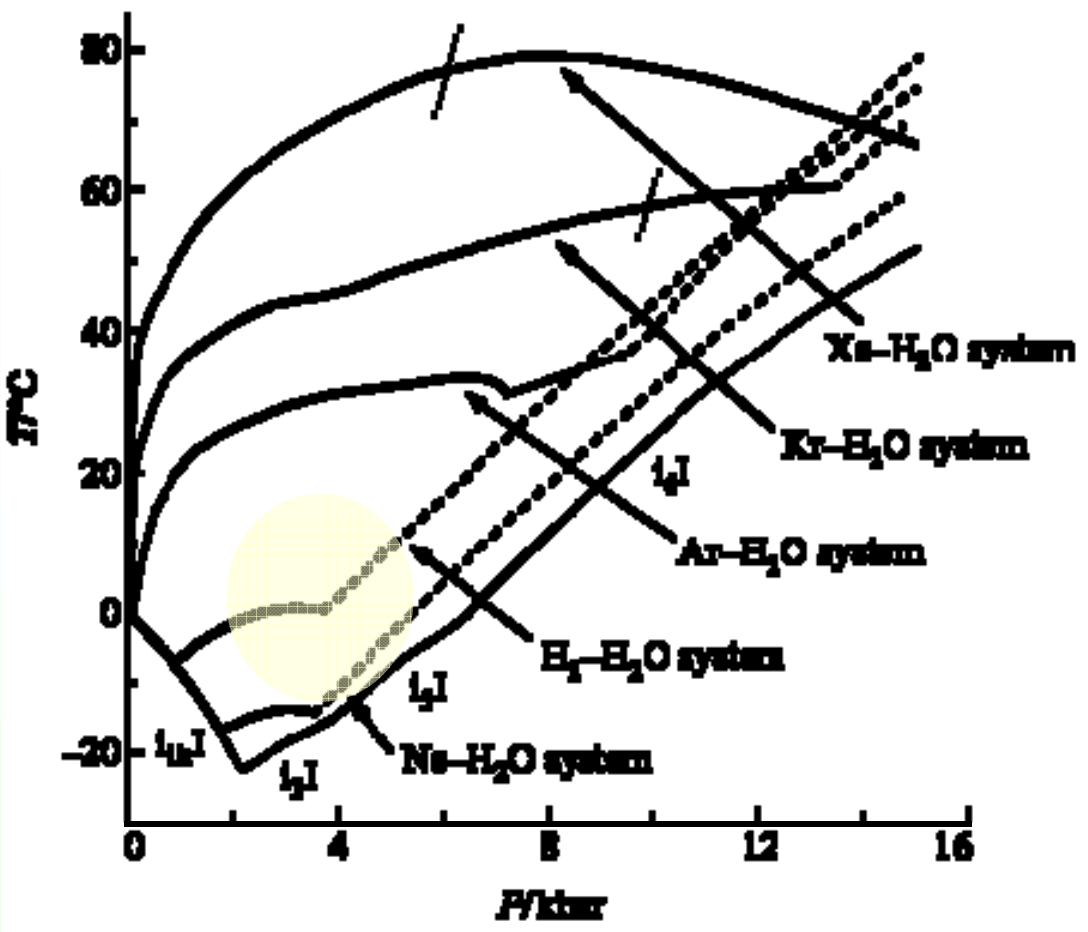
Lokshin et al. *Rev. Sci. Instrum.* 76, (2005) 063909

Applications of the setup for clathrate hydrate investigation

- ✓ **Detailed structure information**
- ✓ **Phase diagram investigation**
- ✓ **Kinetics of formation and decomposition**

H_2, Ne, Kr, Xe, CH_4 clathrates studied

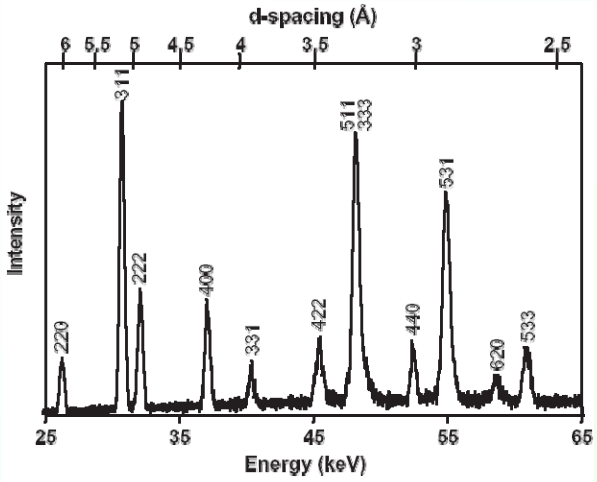
Discovery of hydrogen clathrate hydrate

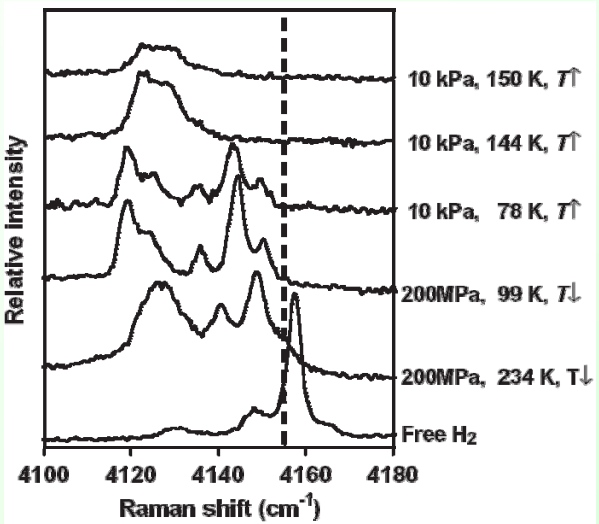


DTA under high pressure

Dyadin et al. *Mendeleev Commun.* **5** (1999) 171

Hydrogen clathrate: characterization (in diamond anvils cell)





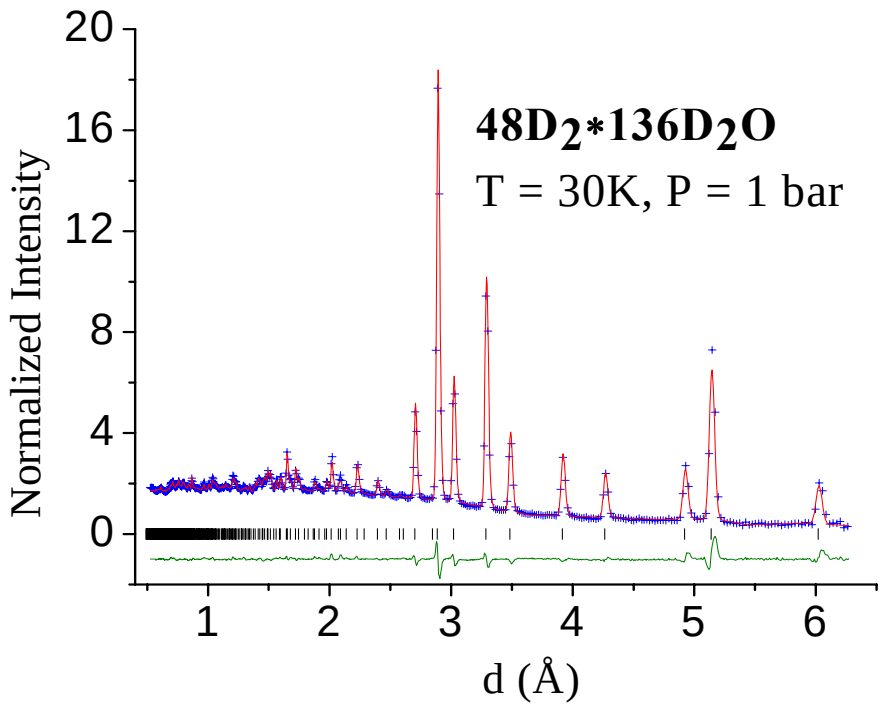
- Synchrotron X-ray diffraction
  Cubic structure II, a = 17.05(1) Å

- Raman spectroscopy

H_2/H_2O molar ratio up to 0.45(5)

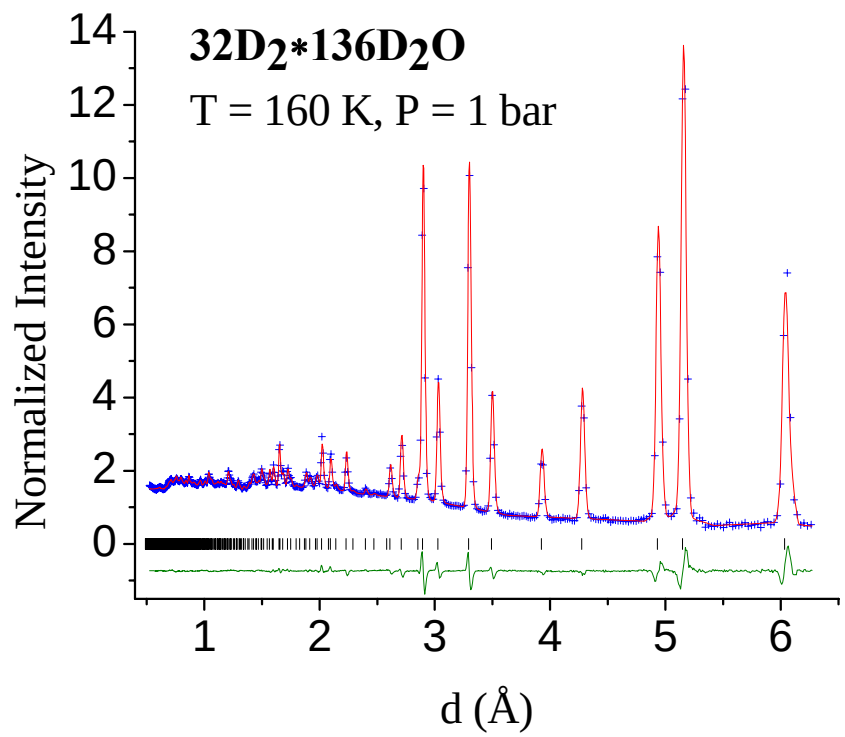
Mao, W.L. et al. *Science* **297** (2002) 2247

Rietveld refinement of neutron diffraction data



D_2O and D_2(gas),

1-2000 bar, 10-300 K

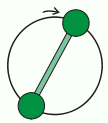


Good fitting parameters

R_p:	3-4%
R_{wp}:	1.5-2.5%
χ^2:	1.8-3.2

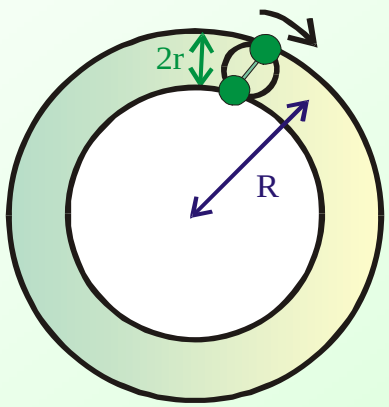
D_2 molecular scattering models (form-factors)

1. Localized D_2 molecule

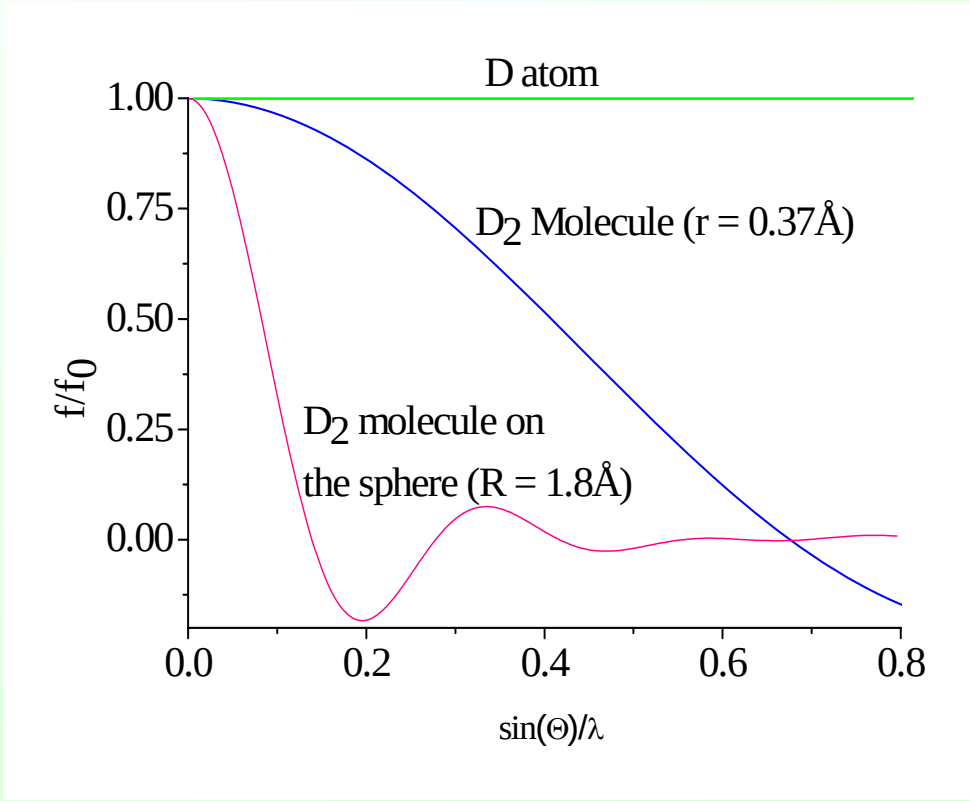


$$f = f_0 \frac{\sin(kr)}{kr}$$

2. Spherically delocalized D_2 molecules (rotator model)

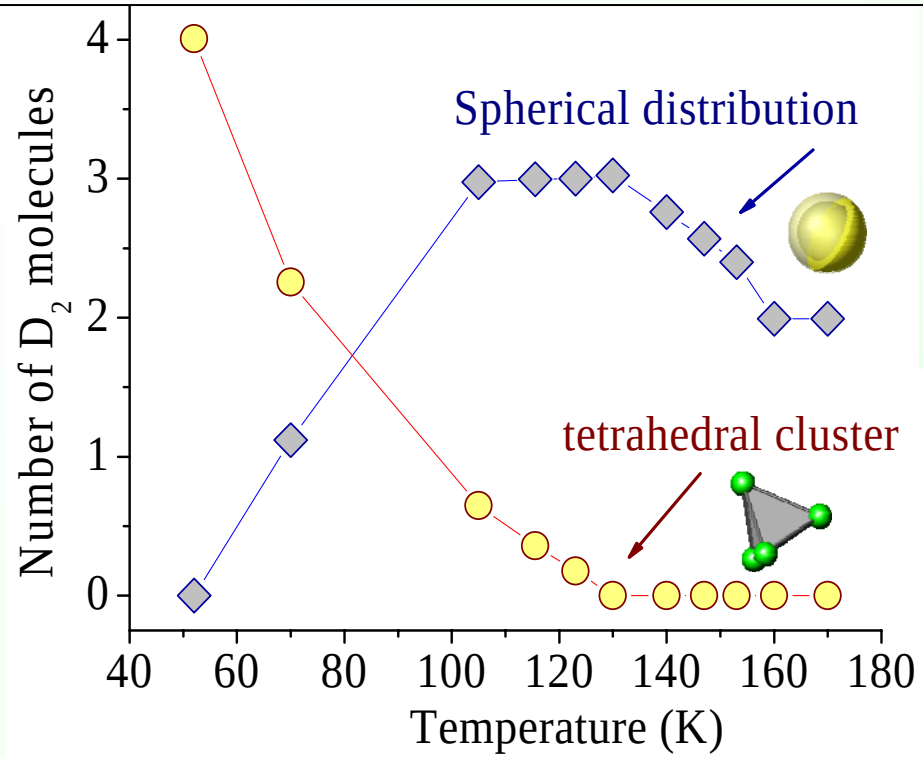


$$f = f_0 \frac{\sin(kR)}{kR} \frac{\sin(kr)}{kr}$$



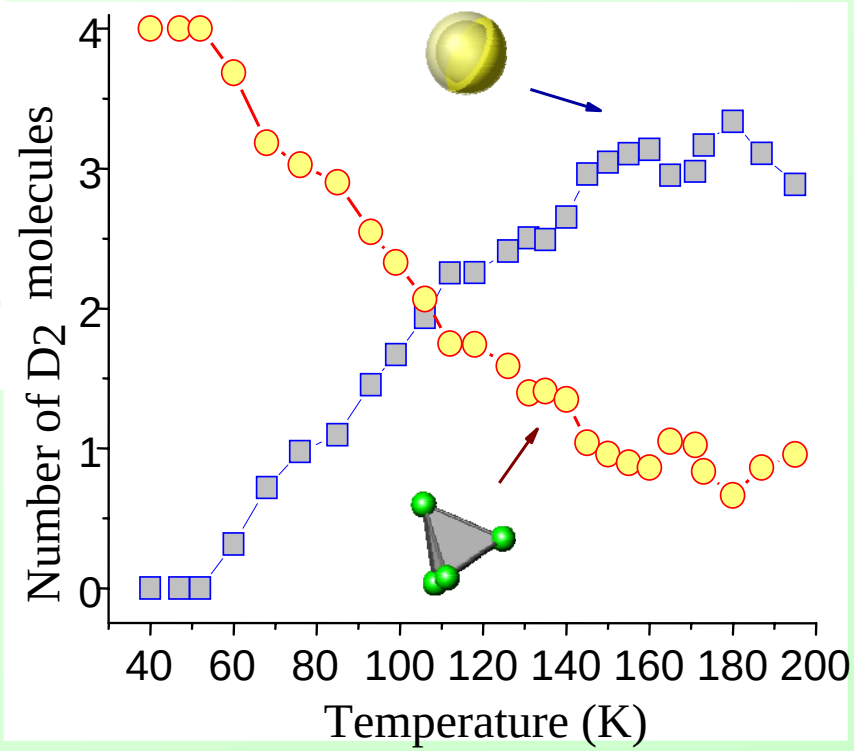
Refinement of hydrogen molecules in cages

(Example: Large cage)



1 bar

Hydrogen distribution refined as a linear combination of ***localized*** and ***delocalized*** models

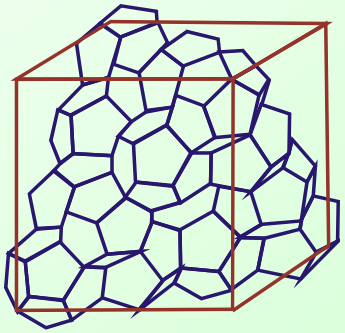


2 kbar

Crystal structure of hydrogen clathrate

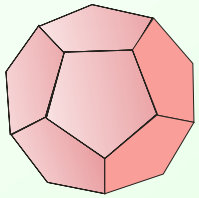
Cubic Structure II at T~10-270K, p~1-2000bar

S.G.: $Fd\bar{3}m$ $a \sim 17$Å

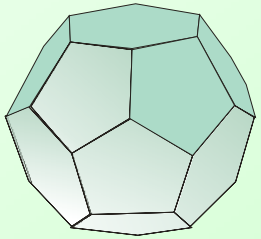


Unit cell: 136 H_2O

$16*(5^{12}) + 8*(5^{12}6^{4})$



(5^{12}) *dodecahedron*

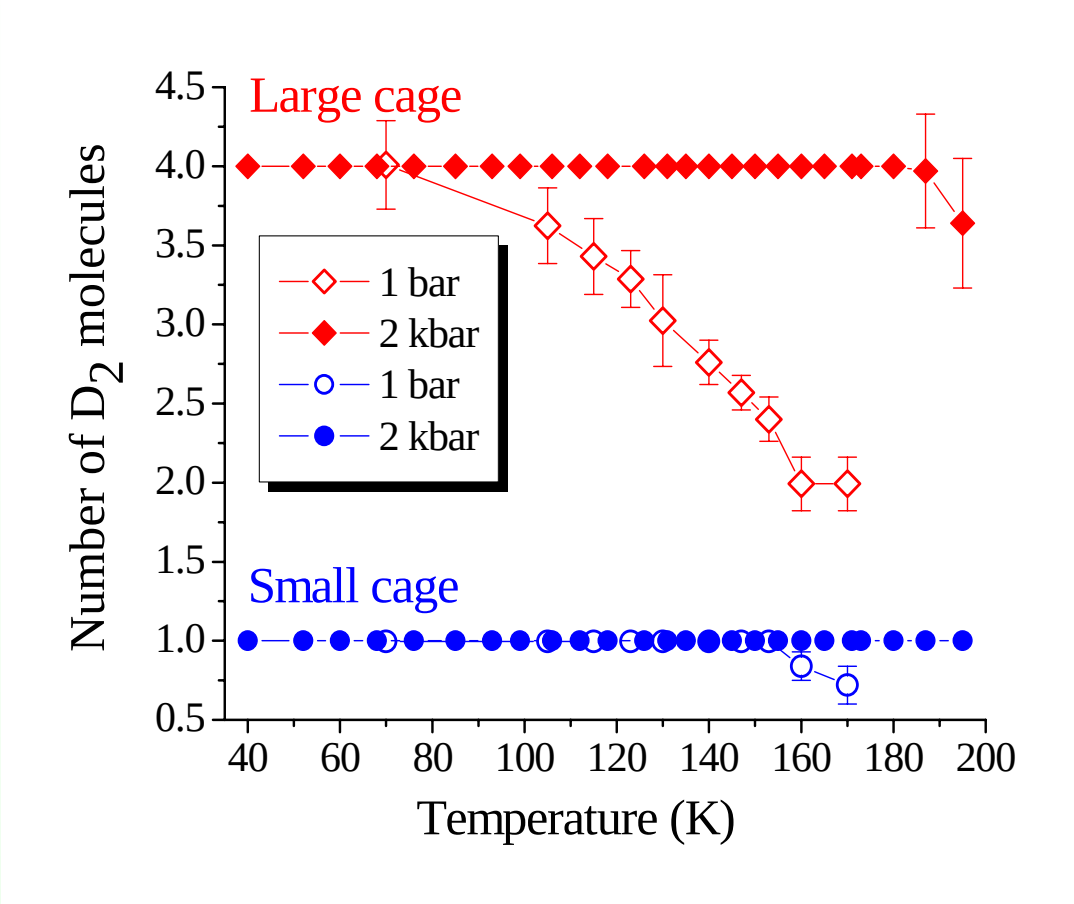


$(5^{12}6^{4})$ *hexakaidecahedron*

Variation of the crystal structure with pressure and temperature:

- **Hydrogen occupancy**
- **Distribution of hydrogen molecules in the cages**

Variation of hydrogen occupancy in the clathrate



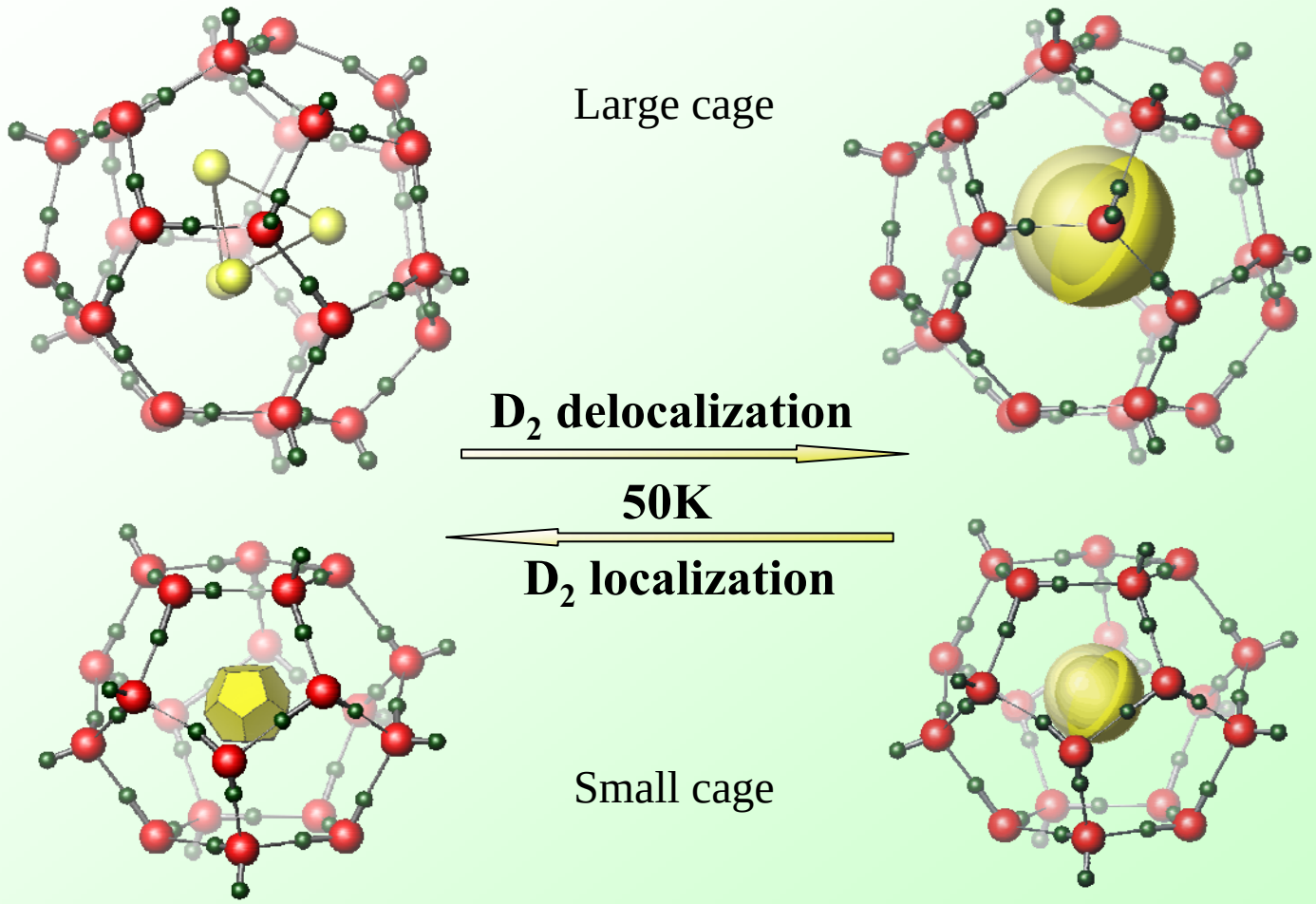
Large cage occupancy varies between 2 and 4 hydrogen molecules

Single occupancy of the small cage at pressure up to 2 kbar

Max. H_2 fraction of total mass = 3.77 %

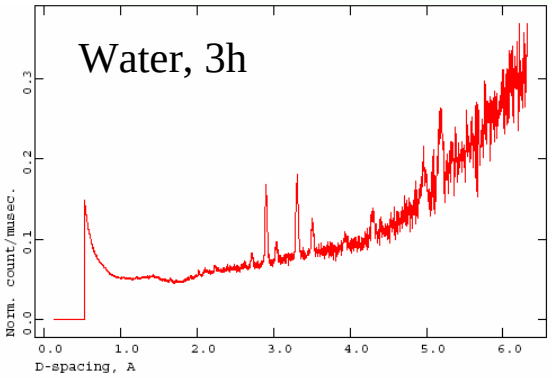
$T_{decomposition}$ = 163(2) K at ambient pressure

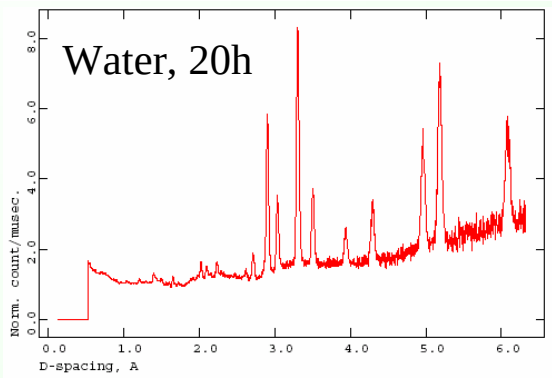
Localization-delocalization of hydrogen molecules

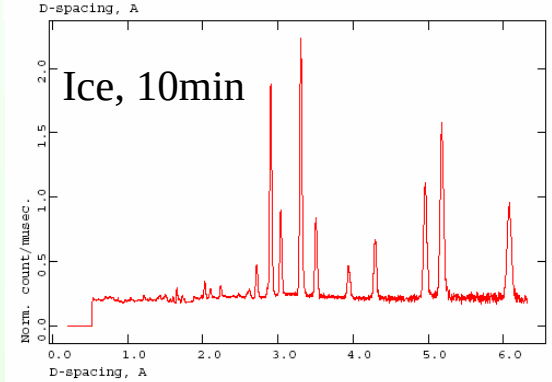


Lokshin K.A. et al. *Phys. Rev. Lett.* **93** (2004) 125503

Ice method for hydrogen clathrate formation







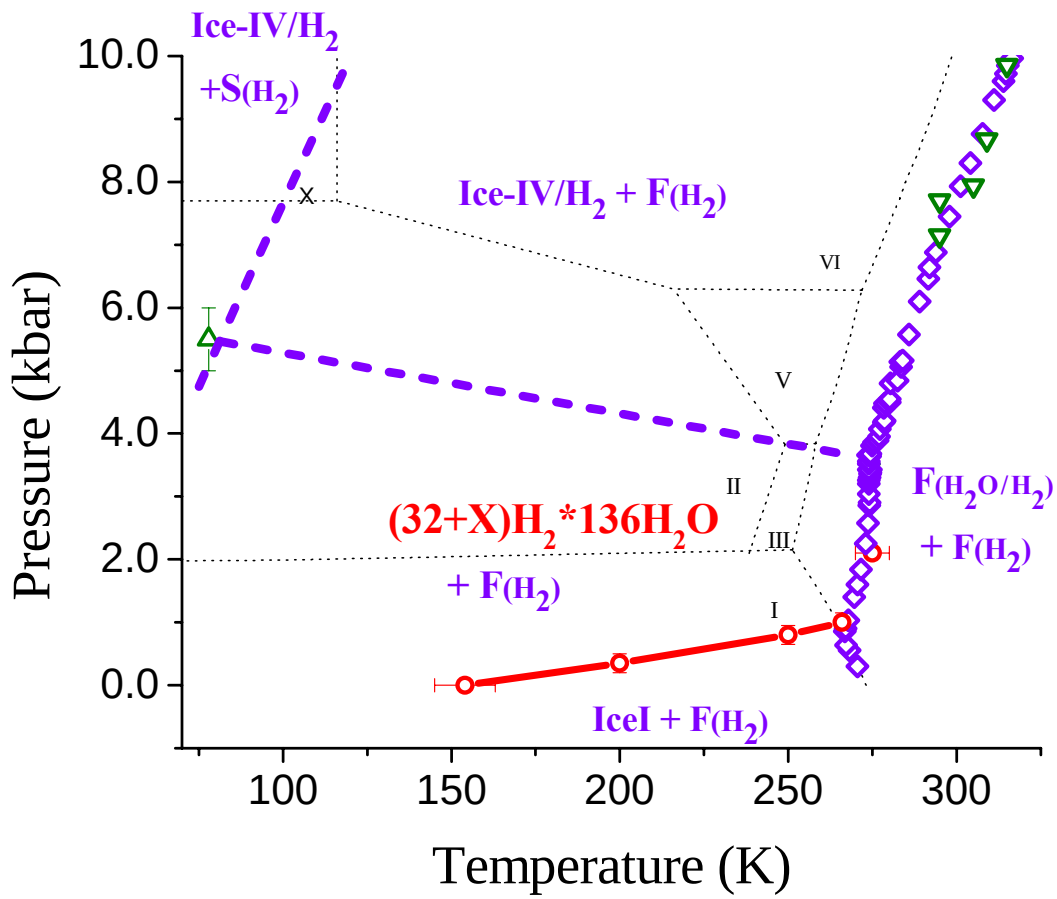
$$H_2(gas) + H_2O(ice) \xrightleftharpoons{10min} 48H_2*136H_2O \quad (p < 500bar)$$

- Fastest clathrate formation at $T \sim T_{(melting)}$.
- No fast formation from amorphous ice.
- Grain size of ice influence on the kinetics. However, even starting from samples with equal surface areas, clathrate formation from ice is still at least 100 faster than from water

Partial penetration of hydrogen into ice cavities could be a mechanism of clathrate nucleation.

Lokshin K.A. & Zhao Y. *Appl. Phys. Lett.*, 2005 (submitted)

H_2-H_2O phase diagram



◊- *Dyadin et al. Mendeleev Commun. 5, 171 (1999)*

∇- *Vos et al. Phys. Rev. Lett. 71, 3150-3153 (1993)*

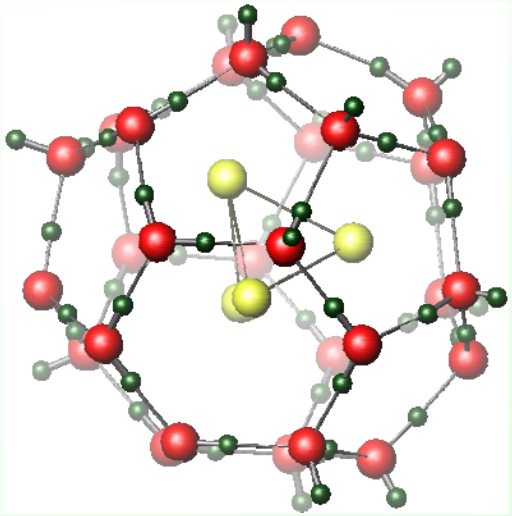
Δ - *Mao et al., Science 297, 2247 (2002)*

O - *our data for (32+X)D_2*136D_2O*

Lokshin K.A. et al. *Appl. Phys. Lett.* (2005) Submitted

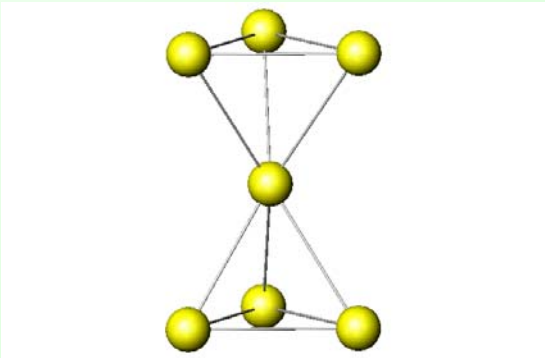
H_2-H_2 distance at ambient pressure

Clathrate hydrate



2.9 Å

Solid hydrogen



3.8 Å

Framework structure affects the local density of guest hydrogen molecules

Conclusions

1. Crystal structure of hydrogen clathrate was determined as a function of pressure and temperature for the first time. Distribution of the guest hydrogen molecules varies with temperature and undergoes localization-delocalization.

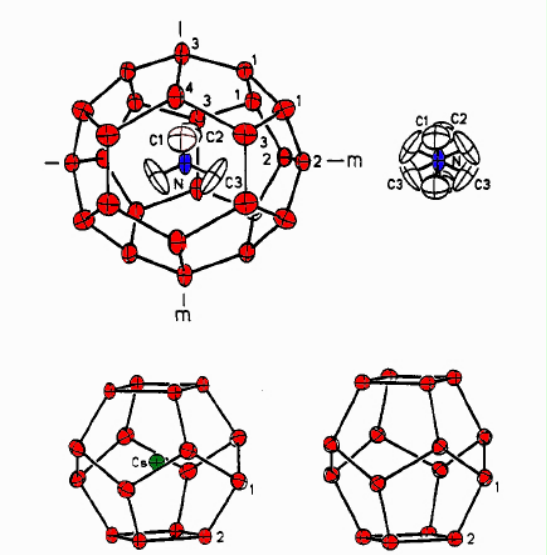
2. Hydrogen occupancy in $(32+X)H_2*136H_2O$, X = 0-16 clathrate varies with temperature and pressure. Maximum H_2 fraction of total mass is 3.77 %.

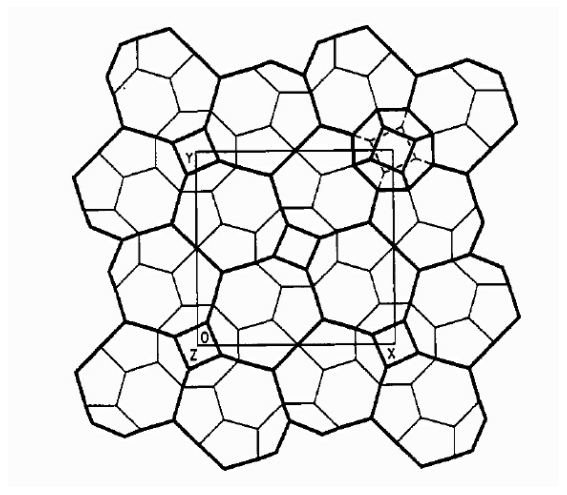
3. Short intermolecular H_2-H_2 distance in the clathrate suggests that inclusion compounds could be a promising hydrogen storage medium.

Future work?

Partial Substitutions affect the thermodynamics:

$Cs(Me_4N)_2(OH)_3 \cdot 14H_2O$ crystallizes at 57 °C compared to the Cs free analogue ($Me_4NOH \cdot 7.5\ H2O$) melting at 4°C





Mootz D. and Staben D., J. Am. Chem. Soc., ***1994****, 116, 4141.*