New structural systematics in the type I and II clathrate hydrate structures at high pressure

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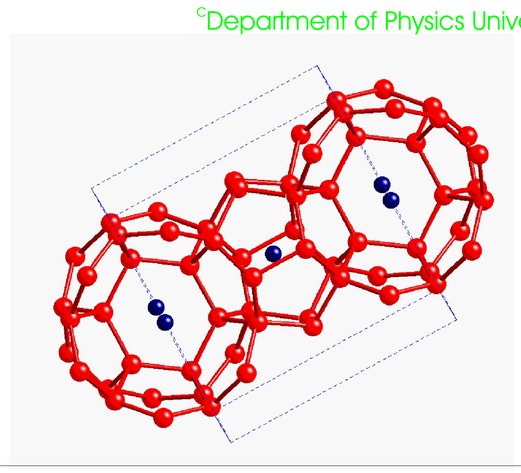
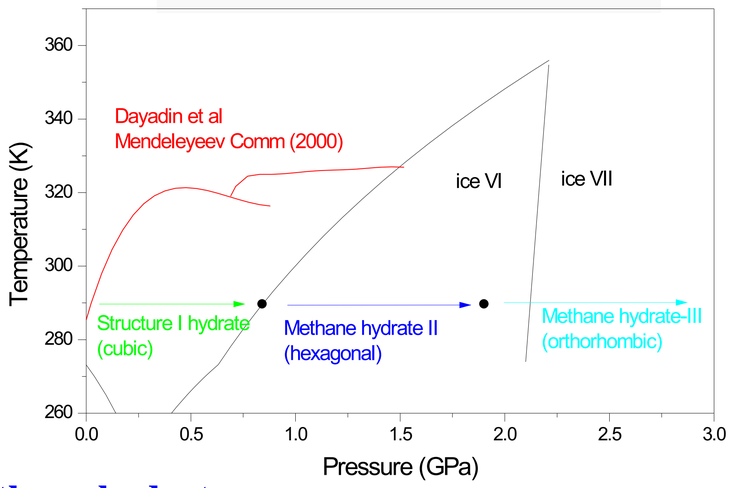




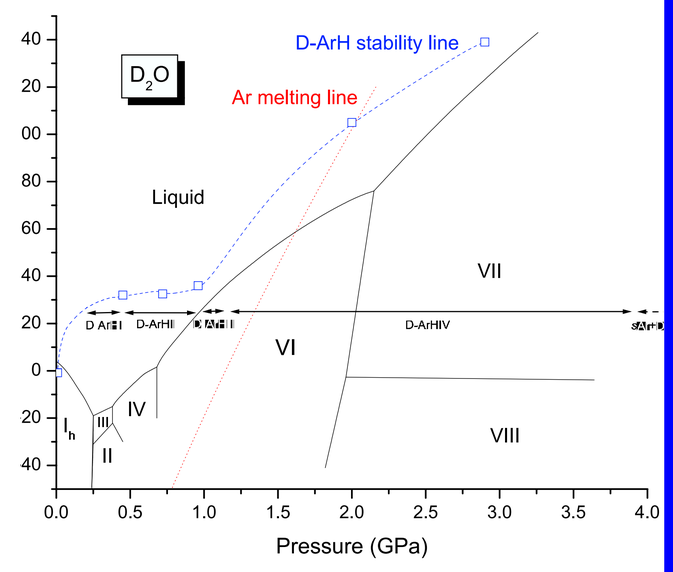
Introduction

The clathrate hydrates are an important group of materials

They are model systems for the study of hydrophobic interaction
Protein folding, species in solution

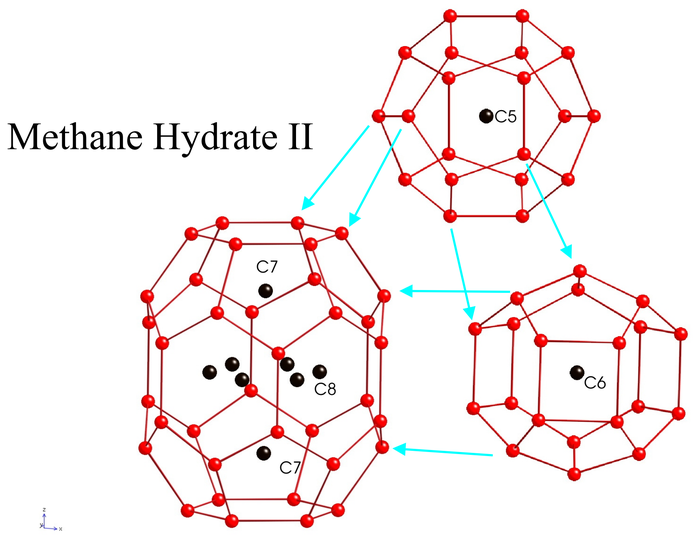
Important to the Earth's climate
Methane hydrate as an energy reserve
Methane hydrate causes catastrophic global warming (in Earth's history and post 2057?)
Carbon dioxide sequestration

Gas bearing ices in outer solar system
The origins of Titan's atmospheric methane



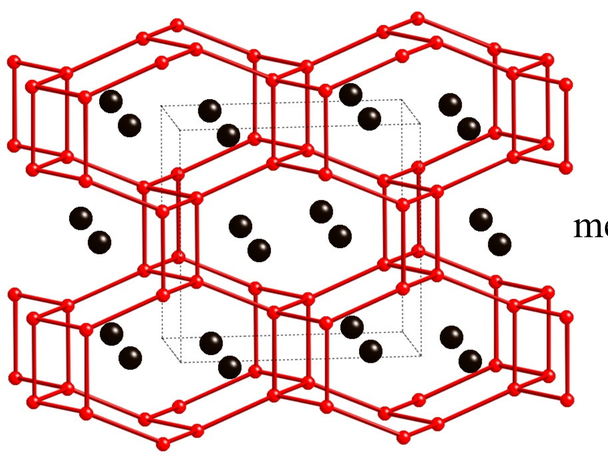
Methane hydrate (Loveday, Nelmes Guthrie, Belmonte Allan, Klug Tse and Handa Nature 2001)

Two high pressure hydrates
Methane hydrate II (hexagonal)
Methane hydrate III (orthorhombic)



Methane hydrate II

Clathrate-H structure
two small and one large cage
One methane in each small cage (five in total)
Five molecules in the large cage (C8 sites half occupied)
Overall 3.4:1 water:methane (Phase I 5.6:1)
C...O in small cages 3-7-.39 Å (like cubic low-P structure)
C...O and C...C in large cage V short (3.3-3.4 Å)
C...O like MH-III C...C shorter than in MH-III or methane
Very densely packed
Why does methane agglomerate into phase II and then disperse again to form phase III?



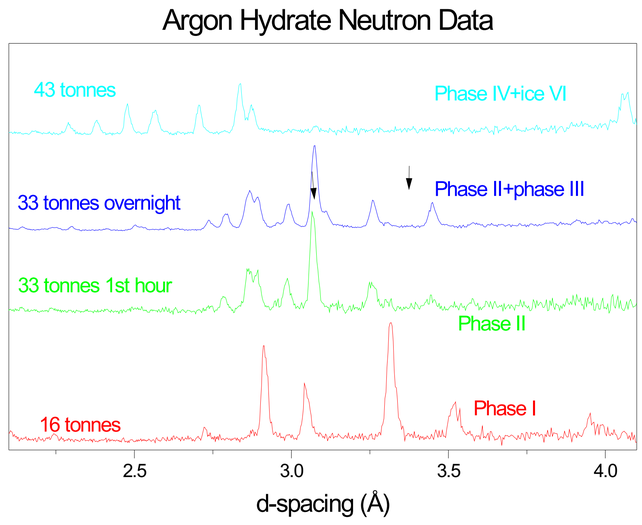
methane hydrate III

Methane hydrate III (Loveday, Nelmes, Guthrie, Klug and Tse PRL 2001)

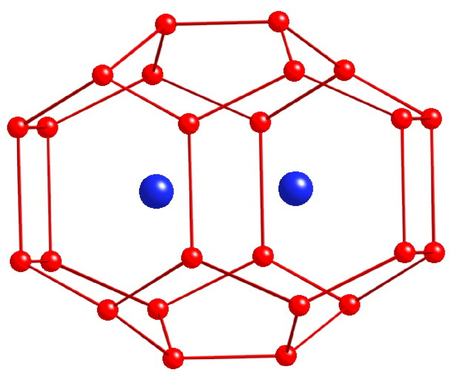
Orthrhombic (Ibmm)
Not a cage clathrate
Network related to ice Ih
One H bond changed to open up channels for methane
Filled ice like hydrogen and helium hydrates

Argon hydrate

Low-p cubic structure II clathrate (methane hydrate structure I)



Similar transition sequence
0.5 GPa structure H+water (Manakov et al 2002)
Turns to new phase with time
Either metastable or on cooling overnight (Tc close to RT)
New phase tetragonal 3:1 water: methane ratio
at ~1 GPa transforms to phase-IV
Has MH-III structure

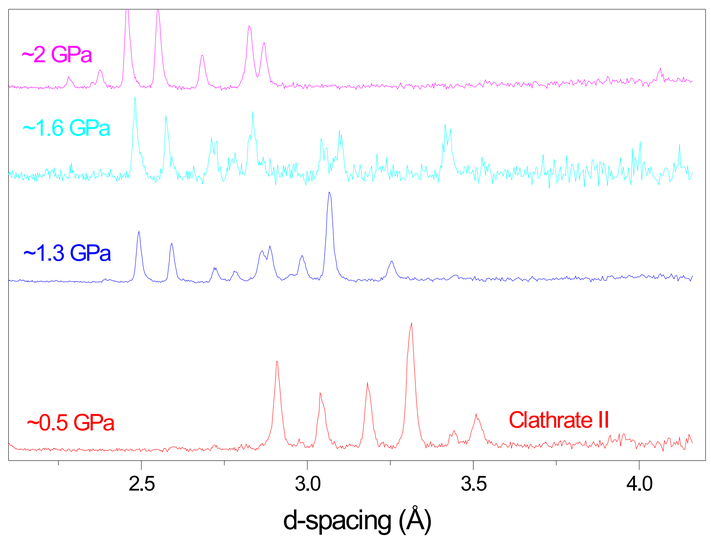


Argon Hydrate III

Nitrogen hydrate

Again cubic structure II at low-P
Phase transition at 0.8 GPa

Further transition at ~1.6
Further transition at ~1.8 GPa



Structural systematics

Broadly the same systematics Cubic—Structure H— Filled ice Ih (same for N2?)
Structure II clathrates include tetragonal cage structure why not methane hydrate?
Trend is to use less water to surround gas with increasing pressure
Cubic structures ~5.5:1, Structure H 3.5:1, Tetragonal 3:1, Filled ice Ih 2:1
Trend to go from dispersed gas to clumped and tightly packed in structure H and then back to dispersed gas in the dihydrate
Same trends in all three systems but xenon water is different (see poster by Serge Desgreniers)

What happens at higher P?