Investigating the Metastability of Clathrate Hydrates

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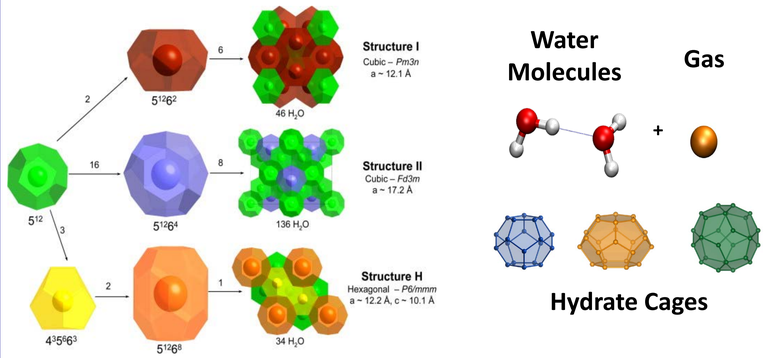
Introduction

What are Hydrates?

Clathrate hydrates or 'gas hydrates' are ice-like inclusion compounds that form from water and suitably sized 'guest' molecules. Depending on guest size, typically 1 of 3 common structures are formed.



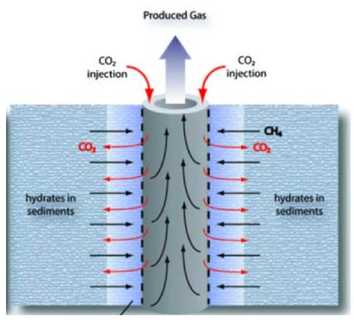
Strobel et al., *Chem. Phys. Lett.* **478**, 97, (2009)

Hydrates for Energy Applications

Clathrate hydrates are currently studied for a host of different energy applications including:

- Energy Storage
- Energy Transportation
- CO_2 Sequestration

Image Courtesy of P. Walz, MBARI



Koh et al., *Appl. Phys. Rev.*, **106**, 061101, (2009)

Hydrate Metastability

Hydrate metastability is poorly understood and is prevalent during synthesis, formation, and dissociation. Metastable hydrates have the potential to impact many energy applications in the form of:

- Existence at thermodynamically unstable conditions
- Formation of unstable structural phases
- Unusual cage occupancy for a particular cage

Understanding these metastabilities and the synthesis-structure-stability relations is critical to the successful application and control of hydrates for all energy applications.

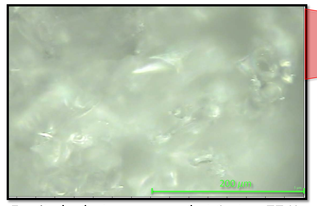
NGH Hydrate Pellets 'Self Preserved' at 1 atm, -20 °C

Image Credit - http://mes.dande-lion.co.jp/english/mes_technology/ngh.html

Experimental Tools and Techniques

Primary characterization techniques include:

- Raman Spectroscopy
- Powder X-ray Diffraction
- ^{13}C and ^{1}H NMR



Ex-situ hydrate preserved at 1 atm, 77 K

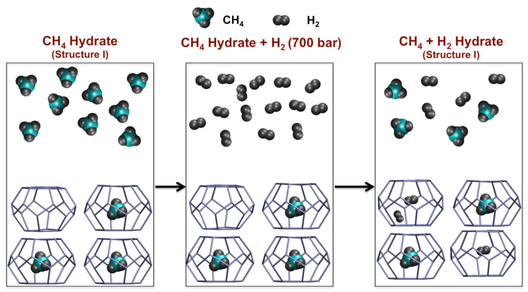
LabRAM HR confocal Raman with cooling stage

Hydrate Metastability in Experiments

Changing the Hydrate Synthesis Pathway

Conventional hydrate synthesis pathway consist of 3 distinct steps:

1. Mix water and hydrate former(s)
2. Implement driving force (low temperature / high pressure)
3. After induction period, most thermodynamic structure is formed

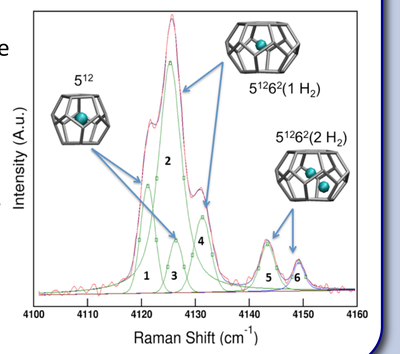


Using a new synthesis technique, can 'force' guests to occupy many different structures, not just the thermodynamic stable structure.

Hydrogen Occupancy in Structure I (sI)

By repressurizing a preformed sI hydrate (CH_4) with H_2 (shown above), we show the first experimental evidence of H_2 in both the small and large cages of sI.

Serves as proof of concept for synthesis method and may be applied to new structures and guests in the future.

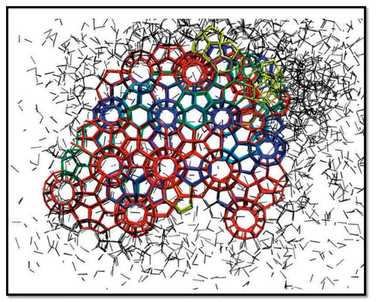


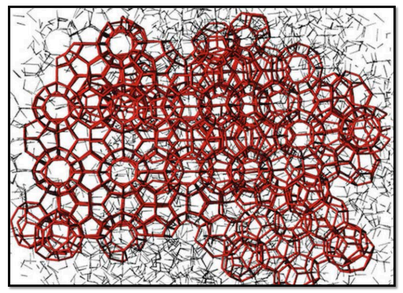
Hydrate Metastability in Simulations

Metastable Cage Clusters

CH_4 hydrate nucleation studies have shown that at high driving forces, a kinetic product of metastable cage clusters can initially form (left).

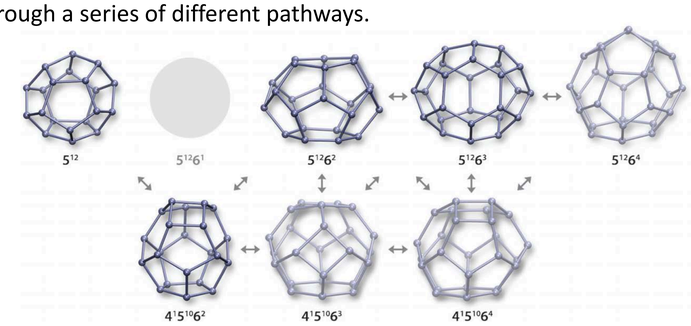
Over time as the initial structure begins to anneal, cages can transition to the thermodynamically stable product (right).





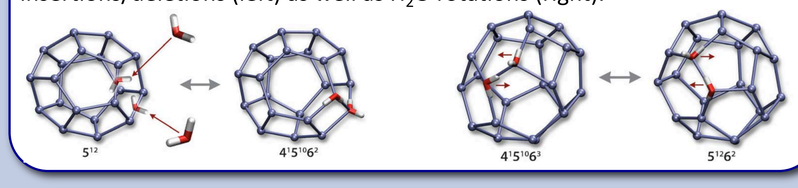
Cage Transition Pathways

The conversion from metastable to stable cage types was observed through a series of different pathways.



Cage Transition Mechanisms

Two prominent mechanisms for the observed cage transitions were H_2O insertions/deletions (left) as well as H_2O rotations (right).



Conclusions

- Understanding hydrate metastability is important for all energy applications of hydrates.
- Hydrate synthesis pathways may be tailored to form metastable structures/cage occupancies which may allow for greater storage.
- During hydrate nucleation, metastable cage clusters can form and then anneal to thermodynamically stable structures through various pathways.

Acknowledgements

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