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.

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.

Experimental Tools and Techniques
Primary characterization techniques include:
- Raman Spectroscopy
- Powder X-ray Diffraction
- $^{13}$C and $^{1}$H NMR

Hydrate Metastability in Experiments

Hydrate Metastability in Simulations

Metastable Cage Clusters

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

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.

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