Investigating the Metastability of Clathrate Hydrates for Energy Storage

PI: Carolyn A. Koh, co-PI: Amadeu K. Sum
Colorado School of Mines, Center for Hydrate Research
Chemical and Biological Engineering Department, 1600 Illinois Street, Golden CO 80401
ckoh@mines.edu, 303-273-3237

Administrative Point of Contact name, email, telephone number:
Monica Hensen, Grant Administrator, Office of Research Administration,
mhensen@mines.edu, 303-834-2186

Funding Opportunity FOA Number: DE-FOA-0000995
DOE/Office of Science Program Office: DOE – Basic Energy Science – Material Synthesis and Processing Science

DOE/Office of Science Program Office Technical Contact:
Program Manager: Bonnie Gersten

DOE Award Number (if Renewal or Supplemental Application):

Final Report of DOE-BES Award DE-FG02-05ER46242
(9/1/2005 – 8/14/2014)

DOE – Basic Energy Science – Material Synthesis and Processing Science

Proposal Renewal of DOE-BES Award DE-FG02-05ER46242

Program Manager: Bonnie Gersten

Investigating the Metastability of Clathrate Hydrates for Energy Storage

PI: Carolyn A. Koh & co-PI: Amadeu K. Sum, Colorado School of Mines

Final Report Summary of Accomplishments from the DOE Award (9/1/2005 – 8/15/2014)

Important breakthrough discoveries have been achieved from the DOE award on the key processes controlling the synthesis and structure-property relations of clathrate hydrates, which are critical to the development of clathrate hydrates as energy storage materials. Key achievements include: (i) the discovery of key clathrate hydrate building blocks (stable and metastable) leading to clathrate hydrate nucleation and growth; (ii) development of a rapid clathrate hydrate synthesis route via a seeding mechanism; (iii) synthesis-structure relations of H_2 + CH_4/CO_2 binary hydrates to control thermodynamic requirements for energy storage and sequestration applications; (iv) discovery of a new metastable phase present during clathrate hydrate structural transitions. The success of our research to-date is demonstrated by the significant papers we have published in high impact journals, including Science, Angewandte Chemie, J. Am. Chem. Soc.

Intellectual Merits of Project Accomplishments:

The intellectual merits of the project accomplishments are significant and transformative, in which the fundamental coupled computational and experimental program has provided new and critical understanding on the key processes controlling the nucleation, growth, and thermodynamics of clathrate hydrates containing hydrogen, methane, carbon dioxide, and other guest molecules for energy storage. Key examples of the intellectual merits of the accomplishments include: the first discovery of the nucleation pathways and dominant stable and metastable structures leading to clathrate hydrate formation; the discovery and experimental confirmation of new metastable clathrate hydrate structures; the development of new synthesis methods for controlling clathrate hydrate formation and enclathration of molecular hydrogen.

Broader Impacts of Project Accomplishments:

The molecular investigations performed in this project on the synthesis (nucleation & growth)-structure-stability relations of clathrate hydrate systems are pivotal in the fundamental understanding of crystalline clathrate hydrates and the discovery of new clathrate hydrate properties and novel materials for a broad spectrum of energy applications, including: energy storage (hydrogen, natural gas); carbon dioxide sequestration; controlling hydrate formation in oil/gas transportation in subsea pipelines. The Project has also enabled the training of undergraduate, graduate and postdoctoral students in computational methods, molecular spectroscopy and diffraction, and measurement methods at extreme conditions of high pressure and low temperature.

Final Report (9/1/2011-8/14/2014)

DOE Award Number: DE-FG02-05ER46242
Recipient of Award: Colorado School of Mines
Title of Award: Investigating the Metastability of Clathrate Hydrates for Energy Storage
PI: Carolyn A. Koh, **co-PI**: Amadeu K. Sum

Highlights of Key Project Accomplishments:

A number of important breakthrough discoveries have been achieved from the current project (DE-FG02-05ER46242), resulting in high impact publications. The notable highlights are listed below:

- Discovery of new pathways for H_2 enclathration in non-stoichiometric 'tuning' scenarios.
- First experimental verification of H_2 in structure I large cages increasing overall storage.
- First identification of seven different cage types during structure I methane and carbon dioxide hydrate nucleation from molecular simulations.
- Provided experimental confirmation of metastable intermediate structures during hydrate structural transition pathways.

[1] New Pathway Discovered for Large Cage Enclathration of Hydrogen in the Tuning Method *(Grim et al., J. Chem. Phys. 2012)*

In 2002, Mao et al. demonstrated that H_2 could form a structure II clathrate with the potential for 3.8 wt. % storage at the formation conditions of 220 MPa and 234 K [1]. Later in 2004 [2], we showed that these conditions could be drastically reduced to near ambient conditions of ~5 MPa and 279.6 K by adding an additional 'promoter' molecule such as tetrahydrofuran (THF), but at the cost of reducing the storage capacity to around 1.0 wt. %.

Since these two key discoveries, there has been much debate in the clathrate hydrate community over what is now known as the 'tuning effect' [3-5]. It has been proposed that if the concentration of the second promoter molecule is reduced or 'tuned', it may be possible to leave some of the large hydrate cavities open for H_2 occupancy, but still maintain reduced formation conditions. However, since its inception, the tuning effect has been widely debated with studies by many groups (including ours) suggesting the H_2 storage capacity is independent of the concentration of THF (or other larger promoter molecules; [6-8]). However, in 2009-2010 we (at CSM) reported a new breakthrough solid-solid synthesis method for forming tuned clathrate hydrates of THF/H_2 and reported nearly 3.4 wt.% storage at 72 MPa and 255 K respectively [4,5].

As the tuning effect could be an important tool for all future energy applications of clathrate hydrates, we conducted a series of detailed and systematic experiments on the tuning effect. Specifically, we focused on several key synthesis procedural steps. One particularly prevalent method used by most researchers to preserve clathrate hydrates for analysis (post-synthesis) is to use liquid nitrogen (LN_2) quenching of clathrate hydrates. Our recent study provides new insight into how the use of LN_2 quenching can, in some cases, lead to unexpectedly rapid hydrate growth when in the presence of preformed hydrates or 'seeds', leading to compositions similar to those obtained via a tuning method.

To study the effect of LN_2 quenching, we first formed stoichiometric binary clathrate hydrates of THF/H_2 at 72 MPa / 255 K. After formation, we then added fresh ice to the stoichiometric hydrate, and loaded the mixture into a new high-pressure cell. As tuning experiments are inherently non-stoichiometric mixtures, creating an ice + hydrate mixture would accurately reflect the composition used in tuning procedures. After only 4 hours at 255 K (to ensure thermal equilibrium), we quenched the clathrate hydrate – ice mixture in LN_2.

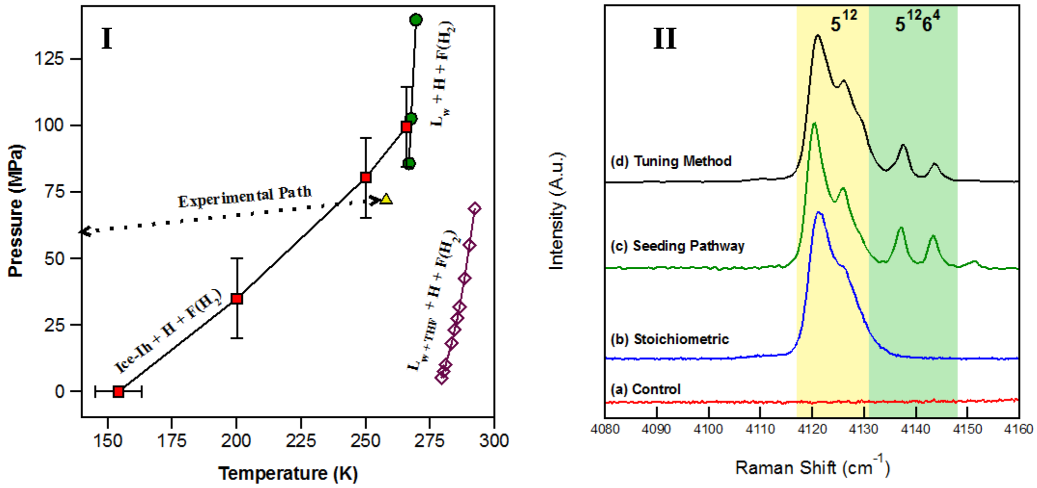


Figure 1 (I): H_2 – H_2O – clathrate hydrate phase diagram. Equilibrium data points were generated from previous work [2,9,10]. Dotted line corresponds to sample conditions during quenching toward LN_2 temperatures. **(II)**: Results of the seeding pathway, highlighting that after quenching ice + preformed hydrates for only 20 minutes in LN_2 (plot C) we observe equivalent results as those obtained using the tuning synthesis procedure (plot D).

As shown in Figure 1-I, as the pressurized clathrate hydrate + ice sample is quenched towards LN_2 temperatures (77 K), it passes into the stability zone for simple H_2 hydrate (dotted line). Although normally this is not considered to be problematic as there is typically no available “free” ice to convert to new hydrate; in tuning experiments, because the amount of promoter molecule is intentionally reduced below the stoichiometric composition (in some cases by 90%), there will inevitably be unconverted ice in the system. Furthermore, it was originally thought that if quenching for only a short period of time (< 20 minutes), crossing into the stability zone might not be important due to the stochastic nature and ‘lag-time’ of clathrate hydrate nucleation. However, we discovered that when ice is present with preformed clathrate hydrates, hydrate “growth” could occur and can have significantly faster kinetics than in the case where seed hydrate crystals are absent.

In Figure 1-II we show the results of our seeding pathway compared to our experiments replicating the previously reported tuning method. Two key results should be emphasized in this figure. Firstly, in a control study where we quenched a sample of pure ice down to 77 K at 72 MPa (the same pressure used in tuning studies), we observed no presence of simple H_2 clathrate hydrate (Fig 1-I.a). This is consistent with the claim that clathrate hydrate cannot ‘nucleate’ after only 20 minutes at these conditions. However, when we added fresh ice to preformed binary clathrate hydrates of THF/H_2, after quenching we observed the presence of H_2 in both the sII small and large cavities, as evidenced by the Raman H-H vibron peaks at 4130 – 4150 cm^{-1} suggesting some of the ice had converted or ‘grown’ into simple H_2 clathrate hydrate. These results show that the presence of preformed clathrate hydrate ‘seeds’ can dramatically increase the kinetics of new clathrate hydrate growth. Additionally, this pathway may play a significant role in the large cage occupancy observed in tuning scenarios.

[2] First Experimental Evidence of Hydrogen in Structure I Large Cage Environments by Novel Synthesis Technique *(Grim et al., J. Phys. Chem. C, 2012)*

Whereas much of the research with H_2 clathrate hydrates has been performed using structure II, recently there have been efforts [11,12] to enclathrate H_2 in other clathrate hydrate structures, such as structure I (sI) and structure H (sH). Although these previous studies have shown that H_2 can occupy these alternative structures, what is noticeably lacking in all of the previous literature is any evidence of large cage occupancy of H_2 in any structure other than sII. Large cage occupancy for H_2 (and other gases) is vital for all energy applications of clathrate hydrates and is best highlighted by previous work from Strobel et al. [13]. Specifically, previously calculated storage capacities illustrate that without large cage occupancy, the H_2 storage capacities of most known structures (sI – sVII) range from 0 – 1.5 wt.%. Conversely, if large cage filling of these structures is achieved, storage capacities can increase to a range of 3.2 – 7.2 wt.%.

In our recent work we demonstrate a clathrate hydrate synthesis pathway that allows for the enclathration of H_2 in the small and large cage environments of sI. In contrast to the traditional clathrate hydrate synthesis method of simply mixing water with an appropriate hydrate former and then implementing a thermodynamic driving force for nucleation by pressurizing/cooling, a new method involving the addition of preformed clathrate hydrates was studied. Using this new technique that we refer to as the "templating method", we prepare a preformed clathrate hydrate and then repressurize the sample to high (> 70 MPa) pressures with H_2 in an attempt to force H_2 to occupy new environments. Therefore, by simply changing the initial hydrate structure (*e.g.* the structure of the preformed hydrate), we can control the final structure, and to some degree, the metastable composition of H_2 in the system.

Raman spectroscopic results of the aforementioned synthesis pathway are provided in Figures 2-I and 2-II. These results show that after pressurizing the sI CH_4 clathrate hydrate with H_2 we observe three distinct H_2 environments at 4121 – 4126, 4125 – 4131, and 4143 – 4149 cm^{-1} respectively. We show for the first time that these environments are not the normally observed sII environments, but rather can be characterized as molecular hydrogen singly and doubly occupying sI cages (Figure 2-II). This key result shows that by altering our synthesis procedure, we were able to observe both small and large cage enclathration in sI and not the thermodynamically preferred structure for H_2 (sII). Additionally, although sI has a lower theoretical storage capacity than the sII H_2 clathrate hydrate, this work serves as proof-of-concept for novel large cage filling, and in the future may be applied to more favorable structures (e.g., sVI). We also expect that this exciting result is likely not unique to H_2 systems and could possibly be extended to other guests, such as CH_4 / CO_2, and could have important implications in all clathrate hydrate related energy applications.

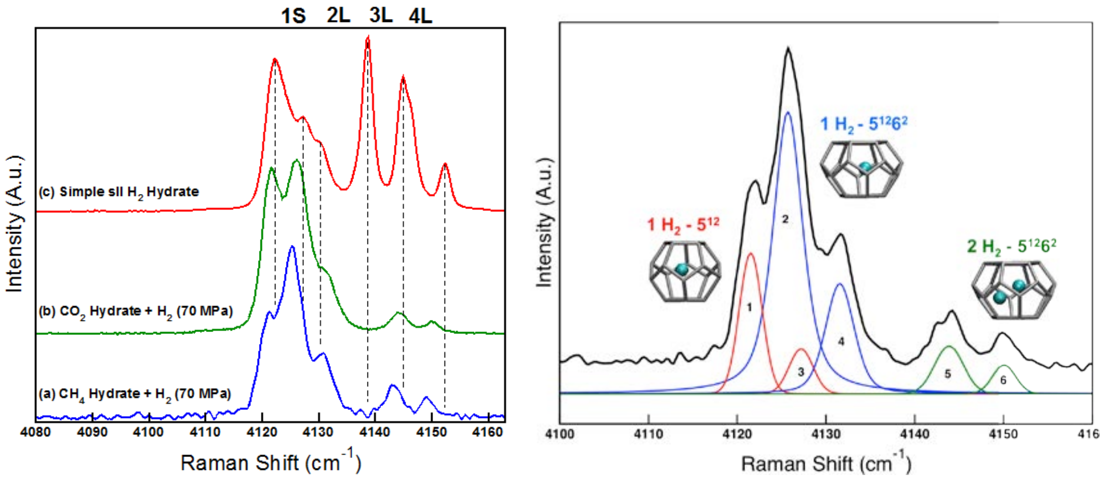


Figure 2 (I): H-H vibron region for (a) CH_4 hydrate repressurized with H_2, (b) CO_2 hydrate repressurized with H_2, and (c) simple sII H_2 hydrate for reference. **(II):** Mixed Gaussian Lorenzian deconvolution shows three unique environments of enclathrated H_2 which are assigned as single occupancy of the small cage and single + double occupancy of the large cage respectively.

[3] Identification of Key Molecular Building Blocks During Clathrate Hydrate Nucleation *(Walsh et al., Phys. Chem. Chem. Phys., 2011)*

To undergo solid-solid rearrangements (*cf.* solid-solid synthesis pathways), our recent simulations have shown several different pathways are possible. Molecular dynamics simulations provide a means of probing key molecular-level clathrate hydrate mechanisms that may be impossible to measure with experiments [14]. Specifically, to transition from a metastable configuration to the thermodynamically stable 5^{12} and $5^{12}6^2$ cages, these cages have been observed to undergo water insertion, deletion, or rotation. In one recent study, direct molecular dynamics simulations investigating the nucleation and growth of structure I (sI) CH_4 hydrate has identified metastable clusters and seven common cages during clathrate hydrate nucleation (Figure 3). It was identified that these seven elementary cage types comprise 95% of all cages present in the nucleating trajectories. These seven incipient cages have been also recently confirmed for CO_2 clathrate hydrate nucleation. This suggests that these cages may be present in the initial nucleation stages of all sI hydrates. Furthermore it is possible that many of these incipient seven cages could be also present in sII or other clathrate hydrate nucleation trajectories. Therefore, using this molecular tool we have been able to probe the clathrate hydrate nucleation pathways and rates at metastable conditions.

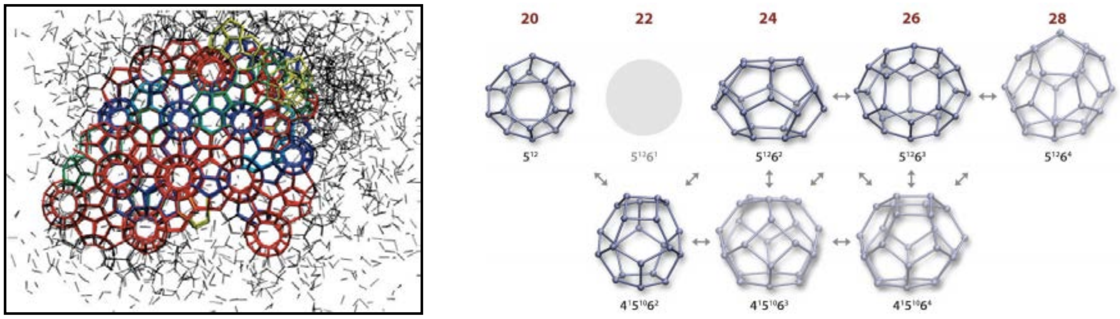


Figure 3. Metastable clathrate hydrate cluster formed during clathrate hydrate nucleation (left). Dominant cages in sI nucleation (right).

[4] Investigating the Thermodynamic Stabilities of Hydrogen and Methane Binary Gas Hydrates *(Matsumoto et al., J. Phys. Chem. C., 2014)*

In evaluating the energy storage potential of a materials often requires a compromise between storage potential and reasonable thermodynamic conditions. Specifically, the materials with the highest storage capacity can have the less favorable thermodynamic (T/P) requirements; while the materials with the most favorable thermodynamics can have the lowest storage capacity. For example, whereas pure hydrogen hydrate can encapsulate 3.8 wt.% of H_2, it requires pressures in excess of 200 MPa for stability. However, when mixed with small amounts of tetrahydrofuran (THF), the conditions required for clathrate hydrate formation can be significantly reduced to around 5 MPa with the tradeoff of only ~1.0 wt.% storage [1-8]. Since our breakthrough discovery of THF + H_2 binary hydrates in 2004 [2], many similar organic promoter molecules have been studied as potential co-guests. However, as mentioned earlier, in addition to reducing formation conditions, these organics tend to completely fill the larger hydrate cavities and reduce the total energy storage capacity of the system. We have recently shown that, like THF, methane (CH_4) could also serve as a thermodynamic promoter, but unlike THF, CH_4 would be small enough that H_2 may compete for occupancy in the larger cages resulting in an overall increase in H_2 enclathration (storage capacity). Furthermore, H_2 + CH_4 binary hydrates have a higher total energy density than H_2 + THF hydrates, because CH_4 serves as an additional source of energy, unlike THF.

When compared to H_2 + THF binary hydrate, hydrates incorporating both H_2 and CH_4 are comparatively underexplored, with some previous work suggesting simultaneous enclathration of H_2 and CH_4 is impossible [15]. In our most recent work, we confirm that not only can hydrogen and methane co-exist in clathrate cages, but they form two types of stable clathrate hydrate structures, structure I and structure II (*cf*. Figure 4, left). Furthermore, in both possible structures, hydrogen was found to occupy both the small and large cages resulting in an overall increase in the hydrogen storage capacity when compared to H_2 + THF binary hydrates. Other important information such as thermodynamic requirements, respective cage occupancies of guest species, and mole fraction in clathrate hydrates were also obtained from ex-situ powder x-ray diffraction (PXRD), Raman spectroscopy, and gas chromatography (GC), respectively.

In Figure 4 (right), we show that the composition of CH_4 and H_2 in the sII hydrate phase is strongly dependent on pressure, with higher pressures resulting in greater fractional occupancy of H_2. On the other hand, the CH_4 mole fraction in the sI hydrate phase is almost constant and is much higher than that of sII hydrate. With the additional energy contained within the enclathrated methane, H_2 + CH_4 clathrate hydrates present a promising potential energy storage medium.

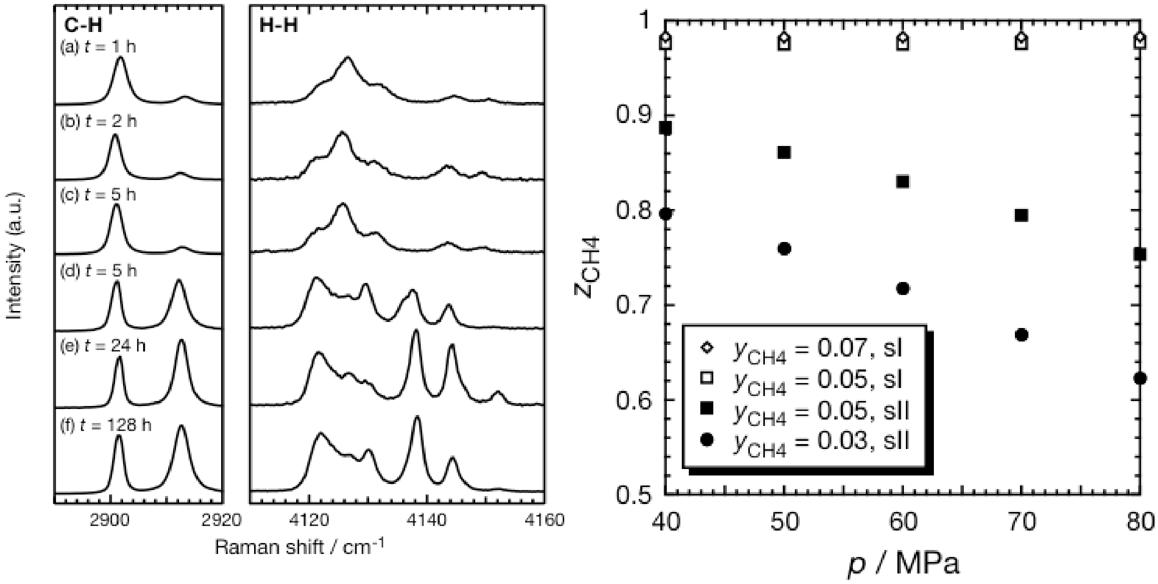


Figure 4. (Left): C-H stretching (left) and H-H stretching (right) frequencies of the methane and hydrogen guest molecules showing the effect of synthesis time on hydrate structure. These results confirm that two separate clathrate hydrate structures (I and II) can form with competition for the small and large cavities from both guests. **(Right):** Hydrate mole fraction as a function of synthesis pressure. These results indicate that from a hydrogen storage perspective, sII will be most favorable, with ~40 mol.% H_2 at 80 MPa and ~20 mol.% H_2 at 40 MPa.

[5] New Quantum Effects Observed for Hydrogen in Clathrate Cavities

When studying clathrate hydrates, the most commonly encountered types of guest molecules are non-polar light hydrocarbons (e.g. methane, ethane, propane). As a heuristic for clathrate hydrate researchers, these light hydrocarbons are often visualized & modeled classically as non-interacting spheres governed by electrostatic interactions and classical mechanics (e.g. Newton's laws of motion). However, when studying hydrogen, these 'rules' can often break down, necessitating a more rigorous quantum mechanical approach. Although the unique quantum-type effects of hydrogen have been extensively discussed for the gas phase and to some extent, the condensed phase, the effect of confinement in clathrate hydrate cavities is comparatively very underexplored. Understanding the physics of confinement inside of clathrate cages is an interesting fundamental question that may provide additional insight into the unique properties of clathrate hydrates.

Molecular hydrogen contains two types of spin isomers, ortho hydrogen and para hydrogen [16]. These two unique spin states are characterized by two Raman peaks separated by roughly 6 wavenumbers (cm^{-1}). In pure hydrogen hydrate (Figure 5.1, left) where hydrogen can singly occupy a small cage and doubly/triply/quadruply occupy a large cage, a set of 8 different Raman peaks (4 different environments x 2 spin isomers) are observed. In Figure 5.1 (left) these environments are labeled individually with the spin isomer type (O or P) and the level of occupancy.

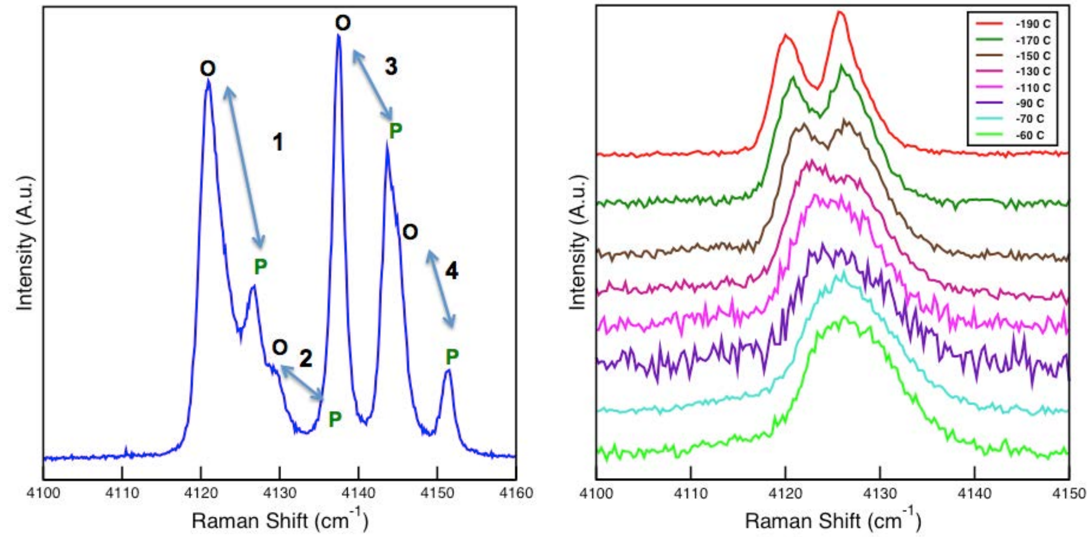
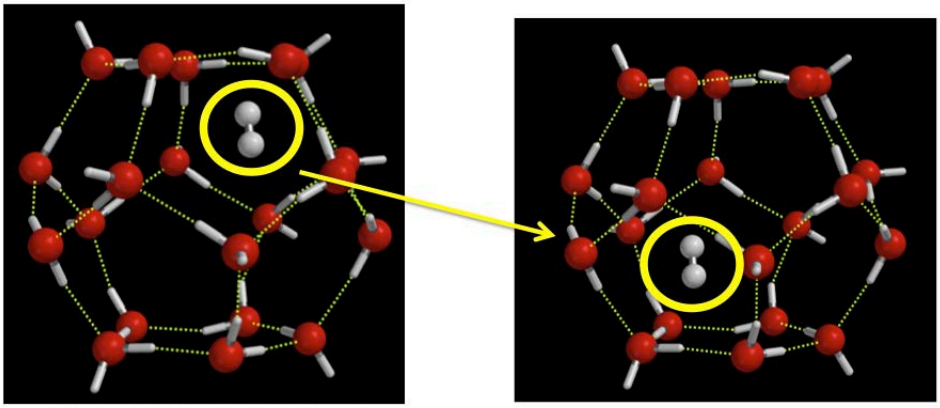


Figure 5.1 (Left): Raman spectrum of pure sII hydrogen hydrate highlighting the 8 different peaks observed due to the multiple levels of occupancy and the ortho-para spin isomers. **(Right):** Raman spectra of binary THF + H_2 hydrate isolating only the small 5^{12} cage contribution. Over the temperature range of -190 to -60 C there is significant broadening of the H-H vibron indicating a significant change in local environment.

We noted that in the pure H_2 spectrum the contributions of the singly occupied 5^{12} small cage (1) seemed to have much poorer peak resolution when compared to the larger cage (2-4). To further explore this phenomenon, we conducted a separate set of experiments studying the effect of temperature on an isolated 5^{12} cage (Figure 5.1, right). We found that by starting from -190 ^{o}C and then slowly warming the sample to -60 ^{o}C, the peak resolution continued to decline, resulting in one very broad peak. There are two potential explanations for these observations. In one scenario, there could be two preferred sites for the hydrogen to rest in the cages, with the first site being preferable at low temperature and the second site becoming more populated at higher temperature (Figure 5.2). Alternatively, a quantum mechanical effect caused by the strong interaction of the rotational and vibrational modes of the hydrogen molecule and the host water modes may cause in this significant broadening.



1 'site' at very low temperature (energy)

2nd site becomes energetically favorable

Figure 5.2: Visual representation of two potential binding sites of hydrogen in the 5^{12} small cage.

[6] Discovery of New Metastable Phase Present During Hydrate Structural Transitions *(Grim et al., Angewandte Chemie, 2014).*

Experiments examining clathrate hydrate structural transition pathways were performed on the structure VI to structure II (sII) transition [17]. It was observed that as sVI clathrate frameworks begin to transition to sII, due to a composition induced change in the equilibrium structure after the addition of H_2 (g), a new intermediate phase was formed prior to the transformation to sII (Figure 6, left). The intermediate environment was studied using in-situ and ex-situ Raman spectroscopy and powder X-ray diffraction, and it was found that the spectral width of the intermediate environment ranged from ~4120 to 4182 cm^{-1}, covering ~62 cm^{-1} (Figure 6, right). The lack of distinct spectral features and relatively large width of the intermediate band compared to the other known structures (Figure 6, right, B-D) suggests that the metastable intermediate states are likely comprised of many unique environments enclathrating molecular hydrogen. To provide a more detailed characterization of these unique environments quantum mechanical calculations with density functional theory (DFT/B3LYP/6-31++G**) were performed to compute the H_2 Raman shifts of all of the stable cages in structures I, II, and VI. Based upon the 62 cm^{-1} Raman peak width of this intermediate environment, in-situ Raman and X-ray analysis, DFT calculations, and comparisons to other known clathrate environments, we show that this intermediate H_2 environment is not consistent with any known thermodynamically stable cage type, suggesting H_2 enclathration is taking place within a metastable clathrate-like intermediate phase.

This recent experimental confirmation of metastable intermediate structures could lead to the potential discovery of an entirely new class of clathrate hydrate structures that, if stabilized, may have potential for energy storage and/or other energy applications. Furthermore, on a fundamental level, the isolation of these metastable transition cages exposes new insight into the clathrate hydrate formation pathways and mechanisms. These new experimental findings are closely aligned with our molecular simulation discoveries of metastable cage dynamics occurring during clathrate hydrate nucleation and growth [18].

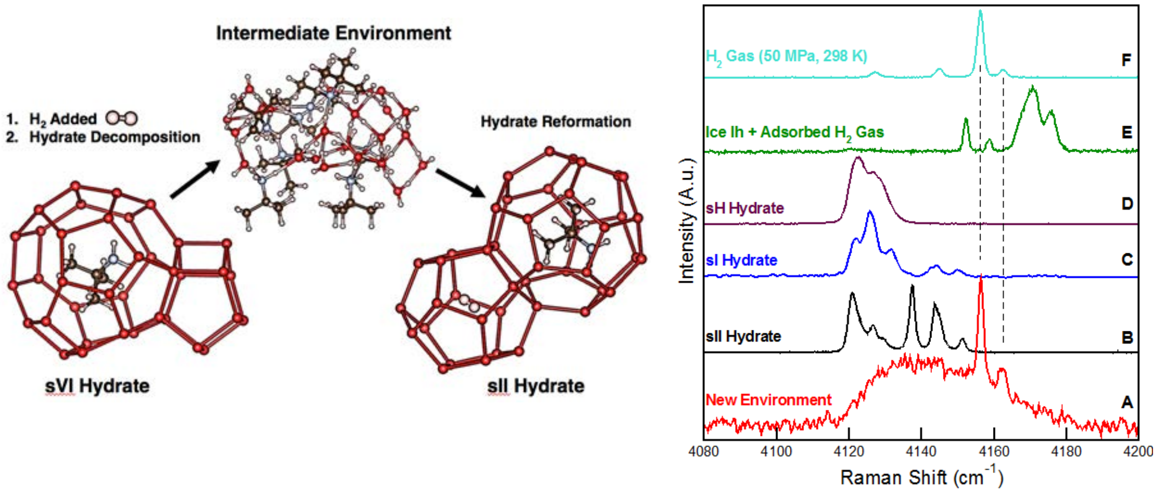


Figure 6. (Left): Suggested pathway for structural transition from sVI to sII after addition of H_2 guest molecule. **(Right):** Raman spectral data of H_2 in known environments of sI, sII, sH, ice Ih, gas phase compared to H_2 in the metastable intermediate environment, highlighting differences in peak position and width. Raman spectra were measured at 0.1 MPa and 118 to 83 K.

Conclusions

In summary, several key scientific discoveries have been made to advance the fundamental understanding on clathrate hydrate nucleation, growth, and structure transition, which can be applied to future systems relating to energy storage and metastability of clathrate hydrates. These discoveries were highlighted by our synthesis and analysis of CH_4+H_2 binary clathrate hydrates, which are suggested to have a higher overall energy density than the extensively studied H_2 + THF systems. Also, our molecular dynamics simulations and DFT theory calculations coupled with experimental confirmation of metastable intermediate structures during clathrate hydrate structural transitions can revise our understanding of clathrate hydrate growth and transition mechanisms. This knowledge will help to advance our understanding of clathrate hydrate dissociation metastability (anomalous self-preservation), which could have exciting implications (for systems containing H_2 and natural gas) for energy storage and transportation at near ambient conditions.

References

[1] "Hydrogen Clusters in Clathrate Hydrate" Mao, W. L.; Mao, H.-K.; Goncharov, A. F.; Struzhkin, V. V.; Guo, Q.; Hu, J.; Shu, J.; Hemley, R. J.; Somayazulu, M.; Zhao, Y. *Science* 2002, *297*, 2247-9.

[2] "Stable Low-Pressure Hydrogen Clusters Stored in a Binary Clathrate Hydrate" Florusse, L. J.; Peters, C. J.; Schoonman, J.; Hester, K. C.; Koh, C. A; Dec, S. F.; Marsh, K. N.; Sloan, E. D. *Science* 2004, *306*, 469-471.

[3] "Tuning Clathrate Hydrates for Hydrogen Storage" Lee, H.; Lee, J.-W.; Kim, D. Y.; Park, J.; Seo, Y.-T.; Zeng, H.; Moudrakovski, I. L.; Ratcliffe, C. I.; Ripmeester, J. a *Nature* 2005, *434*, 743-6.

[4] "Increasing Hydrogen Storage Capacity Using Tetrahydrofuran" Sugahara, T.; Haag, J. C.; Prasad, P. S. R.; Warntjes, A. a; Sloan, E. D.; Sum, A. K.; Koh, C. A., *J. Am. Chem. Soc.* 2009, *131*, 14616-7.

[5] "Large-Cage Occupancies of Hydrogen in Binary Clathrate Hydrates Dependent on Pressure" Sugahara, T.; Haag, J. C.; Warntjes, A. A.; Prasad, P. S. R.; Sloan, E. D.; Koh, C. A.; Sum, A. K. *J. Phys. Chem. C* 2010, 15218-15222.

[6] "Phase Relations and Binary Clathrate Hydrate Formation in the System H_2 - THF - H_2O" Anderson, R.; Chapoy, A.; Tohidi, B. *Langmuir* 2007, *23*, 3440-4.

[7] "Thermodynamic and Raman Spectroscopic Studies on H_2 + Tetrahydrofuran + Water and H_2 + Tetra-n-butyl Ammonium Bromide + Water Mixtures Containing Gas Hydrates" Hashimoto, S.; Murayama, S.; Sugahara, T.; Sato, H.; Ohgaki, K. *Chem. Eng. Sci.* 2006, *61*, 7884-7888.

[8] "Molecular Hydrogen Storage in Binary THF-H_2 Clathrate Hydrates" Strobel, T. a; Taylor, C. J.; Hester, K. C.; Dec, S. F.; Koh, C. A; Miller, K. T.; Sloan, E. D., *J. Phys. Chem. B* 2006, *110*, 17121-5.

[9] "Clathrate Hydrates of Hydrogen and Neon" Dyadin, Y. A.; Larionov, E. G.; Manakov, A. Y.; Zhurko, F. V.; Aladko, E. Y.; Mikina, T. V.; Komarov, V. Y. *Mend. Comm.* 1999, *9*, 209-210.

[10] "Fast Synthesis Method and Phase Diagram of Hydrogen Clathrate Hydrates" Lokshin, K. A.; Zhao, Y. *App. Phys. Lett.* 2006, *88*, 131909.

[11] "Structure and Composition of CO_2/H_2 and $CO_2/H_2/C_3H_8$ Hydrate in Relation to Simultaneous CO_2 Capture and H_2 Production" Kumar, R.; Englezos, P.; Moudrakovski, I.; Ripmeester, J. A. *AIChE Journal* 2009, *55*.

[12] "Water Cavities of sH Clathrate Hydrate Stabilized by Molecular Hydrogen" Strobel, T. A.; Koh, C. A; Sloan, E. D., *J. Phys. Chem. B* 2008, *112*, 1885-1887.

[13] "Hydrogen Storage Properties of Clathrate Hydrate Materials" Strobel, T. A.; Koh, C. A.; Sloan, E. D. *Fluid Phase Equilib.* 2007, *261*, 382-389.

[14] “Microsecond Simulations of Spontaneous Methane Hydrate Nucleation and Growth” M. R. Walsh, C. A. Koh, E. D. Sloan, A. K. Sum, D. T. Wu, *Science* 2009, 326, 1095.

[15] Skiba, S.S.; Larionov, E.G.; Manakov, A.Y.; Kolesov, B.A.; Kosyakov, V.I. *J. Phys. Chem. B* 2007, *111*, 11214–11220.

[16] Strobel, T.A.; Sloan, E.D.; Koh, C.A. *J. Chems. Phys.* 2009, *130*, 014506.

[17] Prasad, P. S. R.; Sugahara, T.; Sloan, E. D.; Sum, A. K., Koh, C. A. *J. Phys. Chen. A* 2009, *113,* 311-315.

[18] Walsh, M. R.; Rainey, J. D.; Lafond, P. G.; Park, D.-H.; Beckam, G. T.; Jones, M. D.; Lee, K.-H.; Koh, C. A.; Sloan, E. D.; Wu, D.-T.; Sum, A. K., *Phys. Chem. Chem. Phys.* 2011, *13,* 951-959.

Progress Report (9/1/2008 - 8/31/2011)

DOE Award Number: DE-FG02-05ER46242
Recipient of Award: Colorado School of Mines
Title of Award: "Molecular Hydrogen Storage in Novel Clathrate Materials"
Principal Investigators: E. Dendy Sloan (PI), Carolyn A. Koh (co-PI)

Highlights of Project Accomplishments:

A number of important breakthrough discoveries have been achieved from the current project (DE-FG02-05ER46242), resulting in high impact publications. The notable highlights are listed below.

- **Breakthrough Synthesis Method** for tuning of binary hydrogen hydrates, achieving increased storage capacity to ~3.6 wt% (Sugahara et al., *J. Am. Chem. Soc.*, 2009 & *J. Chem. Phys. C.,* 2010) [1, 2]. Prior to this breakthrough the maximum storage capacity was ~1 wt% (following on from our paper by Florusse et al., *Science*, 2004).
- **Hybrid Hydrogen Clathrate Structures** synthesized with potential for an order of magnitude storage increase (Strobel et al., *J. Am. Chem. Soc.*, 2008; Shin et al., *J. Phys. Chem. A*, 2009)
- **First Microsecond-Scale MD Simulation** on clathrate hydrate nucleation (Walsh et al., *Science,* 2009).
- **Key Paper on Hydrogen Clathrate Storage** (Strobel et al*., Chem. Phys. Lett*., 2009; cover article)
- **Discovery of Key Clathrate Hydrate Building Blocks** during nucleation (Walsh et al., PCCP, 2011).

Summary of Recent Breakthrough Accomplishments

Over the project period, a number of significant accomplishments have been made at the CSM laboratory, with several high impact journal publications, including papers in Science, J. Am. Chem. Soc., Physics Today, J. Phys. Chem. Some of these accomplishments have been major scientific breakthroughs in the field of hydrogen storage in binary clathrate hydrates [16-21]. The first proof-of-concept was provided to show that two competing molecules can occupy the large cage of sII at the same time [16]. This has led to the tuning concept which can significantly increase the storage capacity of the binary clathrate hydrates (from 1 wt% to 3.6 wt %). It has been shown that the extent to which hydrogen can be enclathrated in the clathrate hydrate is strongly dependent on the formation pressure. Our work has also shown that the hydrate structure can re-enclatharate hydrogen after hydrogen molecules have already diffused out of the structure. The first synthesis of a hydrogen/tetrabutylphosphonium bromide semi-clathrate was achieved. The capacity of this new system was found to be relatively unaffected by variables such as formation pressure, promoter concentration or synthesis pathway. This is in contrast to the binary clathrate hydrates, as it has been shown that the capacity is significantly affected by all of the above variables. This highlights the very different dynamics between the semi-clathrate and the binary clathrate hydrate. This suggests that not all of the science discovered for binary clathrates can be easily transferred to semi-clathrates. Also, molecular simulations carried out at CSM have discovered the first microsecond-scale nucleation pathways for clathrate hydrate formation, as well as the very recent first discovery that seven dominant cage types that occur during sI formation. Such a discovery can potentially lead to new understanding of the kinetics of hydrate nucleation, which can subsequently be applied to enable a better manipulation of the kinetics, which in turn could lead to new structures and materials for the storage of hydrogen, as well as other energy applications of hydrates.

1. First Large Guest Molecular Tuning and Stability of Molecular Hydrogen Binary Clathrates

1.1 Molecular Tuning Region (Sugahara et al., J. Amer. Chem. Soc., 2009)

Work has been performed to show the ability to increase the H_2 storage capacity of a THF/acetone binary hydrate by molecular tuning of the large cage guests, whereby the concentration of the acetone/tetrahydrofuran (THF) is reduced. It has been shown that THF and acetone can act as promoters for the binary H_2 clathrate hydrate by lowering the formation pressure from 220 MPa at 249 K [1] to 5 MPa at 279 K [2]. However, the use of promoters greatly reduces the storage capacity of these binary hydrates from ~4 wt % (for the pure H_2 hydrate) to 1 wt %, as the promoter molecule occupies all of the large cages of the sII clathrate hydrate leaving only the small cages available for molecular H_2 enclathration. Previous researchers' attempts to were unsuccessful in obtaining a higher H_2 capacity by lowering the promoter concentration (below the stoichiometric amount, i.e. lower than 1:17 water:promoter mole fraction), which would increase the amount of large cages available for H_2 molecules, thereby increasing the overall H_2 capacity while maintaining the lower formation pressure [3-6]. In 2009-2010, the CSM laboratory developed a breakthrough clathrate synthesis method, which enabled molecular tuning to be performed for the first time for two promoter large guest molecules, acetone and THF [15,16].

Figure 1. (a) shows the H_2 storage capacity as a function of THF and acetone concentration. The maximum H_2 capacity is reached at around 0.54 – 0.56 mol%. This is about 10% of the stoichiometric ratio (the concentration of THF/acetone needed to completely fill all of the sII large cages) and is referred to as the tuning region. Figure 1. (b) and (c) provide further evidence of the occupancy of the large cage by H_2 though Raman analysis in the hydrogen vibron region. Figure 1. (b) shows that the enclathration of H_2 is taking place because of the presence of the promoter; when the promoter molecule is removed, H_2 is not enclathrated at this pressure. Both Figure 1. (b) and (c) show that at the stoichiometric concentration, intense peaks are observed around 4120 cm^{-1}, with a shoulder around 4125 cm^{-1}. This has been attributed to H_2 enclathration in the small 5^{12} cage [7]. It is not until the promoter concentration is reduced from the stoichiometric ratio towards the

tuning region that peaks are observed around 4140 cm^{-1} and 4150 cm^{-1}. For THF, these peaks start appearing around 0.88 mol% and for acetone around 3.42 mol%. However, the most intense peaks occur in the tuning region of 0.56-0.58 mol% for both promoter molecules. Until the tuning concentration is reached, the promoter molecule was the dominant/only occupant of the large cage. A reduction in the promoter concentration has shown that it is possible for promoter and H_2 molecules to compete for the large cages. Although, the DOE target of 5.5 wt % has not been realized with these systems, it has been shown that the tuning principle can be utilized across different systems, which suggests it can be applied to other systems where it may be possible to reach this DOE capacity target. Farther reaching consequences of this breakthrough discovery is that by tailoring the synthetic pathway to clathrate formation, it can be possible to occupy the large cages with more than one type of guest (promoter + H_2). This was considered not possible before this work.

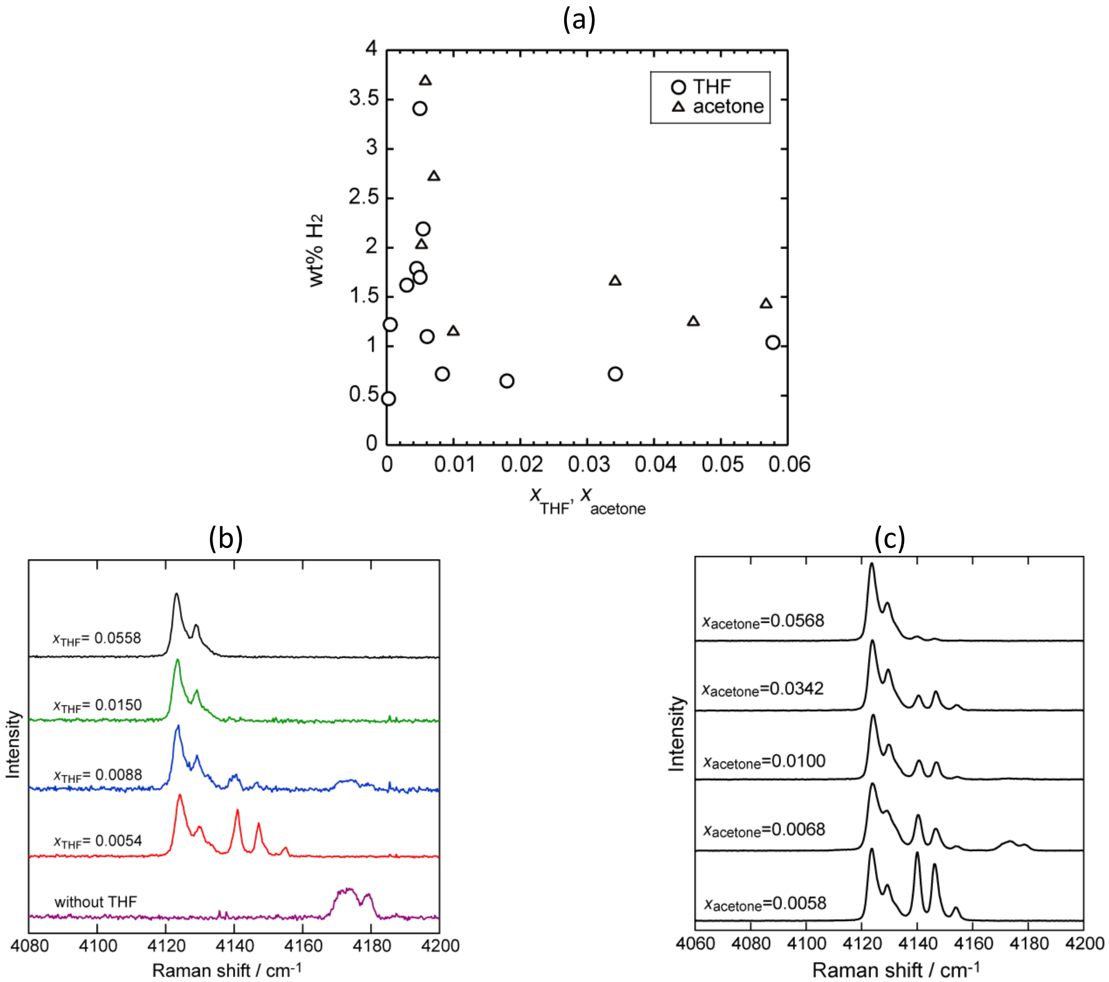


Figure 1: (a) H_2 capacity of THF and acetone binary clathrate hydrates. As the promoter concentration is reduced to the tuning region, H_2 capacity reaches a maximum. (b) and (c) show Raman spectra of H_2 vibrons in THF and acetone binary systems. Peaks around 4120 cm^{-1} show H_2 enclathrated in the small 5^{12} cage. Peaks around 4140 cm^{-1} correspond to H_2 in the large $5^{12}6^4$ cage [15,16].

1.2 H_2 Occupancy Pressure Dependence (Sugahara et al., J. Phys. Chem. C, 2010)

Figure 2 shows how the large cage occupancy is strongly dependent on the formation pressure. Despite the tuning concentration being used in each run, the Raman spectra show large cage occupancy of H_2 only after reaching a formation pressure of around 54-58 MPa. Even at these pressures, the intensity of the peaks suggests that only a small fraction of the large cages are occupied by H_2. It is not until a pressure of 72-74 MPa is used that very intense peaks are observed, which are attributed to H_2 occupancy in the large $5^{12}6^4$ cage. This suggests that even with the majority of the large cages empty and available, a large driving force is required to force the H_2 molecules to occupy the large cages. This further demonstrates that the stability of this clathrate hydrate is not dependent on complete large cage occupancy, another important phenomenon not considered previously for clathrate materials. Indeed the large cage occupancy by H_2 may not be permanent which opens the possibility of longer-term metastability of the clathrate hydrate system, an interesting new approach for increasing the extent of H_2 storage.

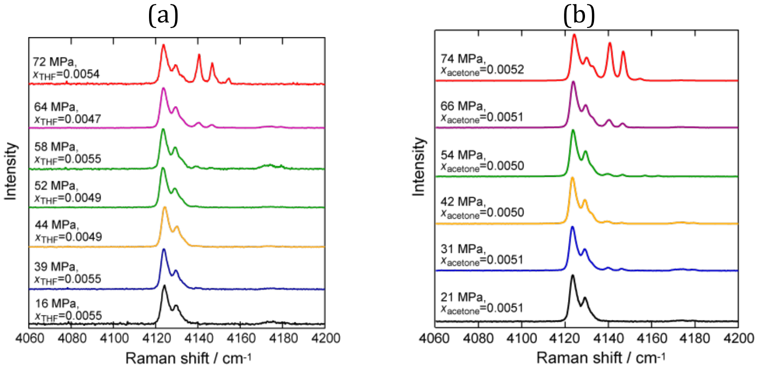


Figure 2: Raman spectra showing large cage occupancy is highly dependent on formation pressure for THF (a) and acetone (b) binary clathrate hydrates.

1.3 Stability/Recyclability of THF/H_2 Binary Clathrate Hydrates

The concept of recycling clathrate hydrates by allowing the release of H_2 from the cages without destroying the hydrate cages was suggested by Ogate et al (2008) [8]. Figure 3 shows Raman and gas evolution measurements demonstrating that the clathrate hydrate structure can be recycled/re-enclathrated without a structural decomposition. The left figure shows the H_2 content measurement of a THF tuning sample after the initial formation. The sample was formed at 60 MPa for 3 days. The capacity was measured to be about 2.9 wt %, showing H_2 occupancy in both the small and large hydrate cages. The sample was then allowed to dissociate at atmospheric pressure and 255 K for 3 days. The decomposed sample had a H_2 capacity of about 0.57 wt %. As it is significantly less than 1 wt % it can be concluded that all of the H_2 molecules have diffused out from the large cages of the hydrate and partially from the small cages. As the large cages have larger faces and molecular connectivity, the H_2 molecules can diffuse out of the large cages more readily than from the small cages. Therefore it is reasonable to assume that all of the large cages would become vacant, leaving only the small cages partially occupied with H_2. The sample was then repressurized to 60 MPa and kept at 255 K for 3 days before being analyzed for a third time. The 'reuse' sample (in Figure 1.3-left) shows the H_2 capacity is greater than the decomposed sample, thus showing that H_2 molecules have reoccupied the cages of the hydrate. The sample shows a capacity which is greater than 1 wt % which suggests that both the small and large cages have been reoccupied with H_2. The Raman vibron spectra (Figure 1.3-right) confirm the interpretation of the gas evolution data. The fresh sample shows H_2 enclathrated in both the small and large cages. In this particular experimental set, the sample was dissociated at 30 MPa for 4 days, which allowed the H_2 to escape from the large cages, while retaining some in the small cages. Once the sample was repressurized, it was evident from the peak positions that H_2 had once again occupied the large cages of the sII clathrate hydrate. Therefore, these studies show that the clathrate hydrate structure can remain intact, and then be reused once H_2 has been released from the cages.

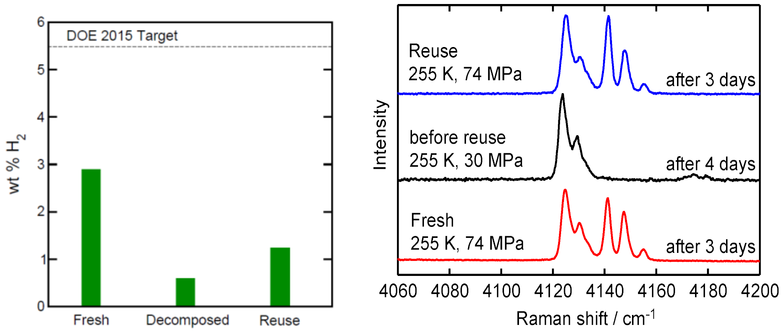


Figure 3: Left - Measurement of molecular hydrogen enclathrated within a THF tuning binary clathrate hydrate. Sample was recycled once. Shows that small and large cages can be reoccupied with hydrogen. Right – Raman spectra of fresh, dissociated and re-used THF tuning sample. Fresh sample shows H_2 in both small and large cages. H_2 in large cages was allowed to dissociate out after 4 days at 30 MPa, and re-filled the large cage after repressurization to 74 MPa.

2. New Molecular Hydrogen Semiclathrate Hybrid Synthesis *(Shin et al., J. Phys. Chem. A, 2009; Yasuda et al., 2011)*

Semi-clathrates have been shown to be able to store guest molecules such as H_2S, CO_2 and so have been suggested by a number of researchers to be capable of storing hydrogen [9-11]. The advantage of the semi-clathrate in contrast to a normal clathrate is that the semi-clathrate, in addition to enclathrating H_2, can also contain H atoms in the host cage network which can be utilized through a hydrolysis reaction. The semi-clathrate due to its unique configuration can be more thermally stable than the true clathrate [12]. Through the hydrolysis reaction the storage capacity of the semi-clathrate/hybrid system could be increased (by around 170 % [13]) compared to the true clathrate, as we demonstrated in 2009 (Figure 4). The ability of semi-clathrates to store H_2 has been explored. Shin et al showed this through Raman spectroscopy and powder X-ray diffraction (PXRD) for Tetra-n-butylammonium Borohydride (TBAB), and Chapoy et al. investigated the stability of TBAB/H_2 and Tetra-n-butylammonium Fluoride (TBAF) H_2 semi-clathrates [11,13].

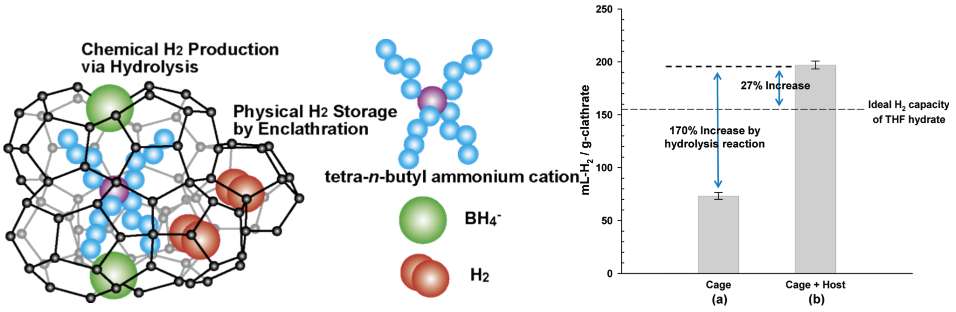


Figure 4. Water cavities with enclathrated TBABh and H_2 molecules. TBA^+ is situated within the large cavities, and BH_4^- replaces a water molecule. H_2 is located in the small cavities. Volumes of H_2 (a) stored in the small cavities and (b) stored in the small cavity and produced via a hydrolysis reaction between water and BH_4 after hydrate dissociation (0.82 atm, 293.15 K).

In very recent work, the tetrabutylphosphoniumbromide (TBPB) semi-clathrate was shown to enclathrate molecular H_2 to produce a new semi-clathrate structure. Table 1 shows the example experiments that were carried out using this semi-clathrate as well as the measured H_2 enclathration, which was measured using gas evolution (with qualitative confirmation from Raman spectroscopy). The different experiments can be categorized into three different groups of investigation; effect of pressure, concentration and formation pathway. The aim was to see if any of these factors could have a significant impact on the H_2 capacity.

Figure 5 provides Raman spectra demonstrating two phenomena – Left: spectra of an ice and H_2 sample, which was pressurized to 60 MPa, compared to a sample composed of ice/TBPB/H_2, also pressurized to 60 MPa. This confirms that the enclathration of H_2, at this pressure, must be due to the presence of TBPB. Right: vibron peaks that correspond to H_2 enclathrated in each of the tests summarized in Table 2.1, except for the ‘tuning’ run. From the pressure runs that were carried out it does not appear that the formation pressure has a very significant effect on the H_2 capacity, at least not in the way it affects the capacity of the THF tuning clathrate hydrate. A 75% decrease in the original formation pressure only corresponds to a 22% decrease in the H_2 capacity, while it corresponds to a 71% decrease for the THF tuning clathrate hydrate. The concentration of TBPB used also does not appear to have a significant affect on the H_2 capacity. The concentration was varied from an excess concentration through to the stoichiometric, down to a very low concentration which was analogous to the clathrate ‘tuning’ region. The H_2 capacity does not vary significantly with a change in concentration until the ‘tuning’ concentration is used. At this point, the H_2 capacity is reduced by about 50%. This severe reduction in capacity is likely because attempts to tune the hydrate, only reduces the amount of TBPB available to make up the host semi-clathrate framework, which would reduce the stability of the hydrogen-bonded lattice.

The other variable that was investigated was the effect of synthesis pathway on the H_2 enclathration. Varying the pathway, included mixing TBPB and water as a solution before freezing and forming the hydrate with H_2. Extending the formation period from 3 to 8 days and refreshing the H_2 atmosphere (templating) after 3 days was also tried. The H_2 capacity did not appear to be severely affected by any of these techniques. On average the H_2 enclathration was about 0.38 wt % for the TBPB semi-clathrate (stoichiometric). Although low, this value is about 3 times the capacity which was predicted by Deschamps et al. [14]. It is evident from these results that the factors that significantly affect the true clathrate hydrate systems, in contrast have little effect on the semi-clathrate system.

Table 1: Experimental summary and measured H_2 enclathration on a wt.% basis for the new TBPB/H_2 semi-clathrate structure

Composition	Pressure	Temperature	Formation Time	Description	Enclathrated H2 (wt %)
TBPB (3.03 mol %)	60 MPa	255 K	3 Days	Base	0.379
TBPB (3.03 mol %)	30 MPa	255 K	3 Days	½ Pressure	0.341
TBPB (3.03 mol %)	15 MPa	255 K	3 Days	¼ Pressure	0.295
TBPB (3.39 mol %)	60 MPa	255 K	3 Days	Excess	0.361
TBPB (1.52 mol %)	60 MPa	255 K	3 Days	½ Stoich	0.381
TBPB (0.76 mol %)	60 MPa	255 K	3 Days	¼ Stoich	0.353
TBPB (0.31 mol %)	60 MPa	255 K	3 Days	Tuning	0.209
TBPB (3.03 mol %)	60 MPa	255 K	3 Days	From Sol	0.325
TBPB (3.03 mol %)	60 MPa	255 K	4 Days	Templating	0.344
TBPB (3.03 mol %)	60 MPa	255 K	8 Days	Extended Time	0.399

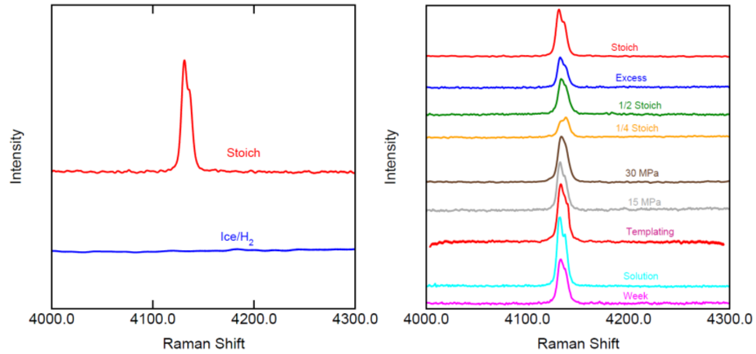


Figure 5: Left – Raman vibron spectrum of ice/H_2, pressurized to 60 MPa, compared to a mixture of TBPB/Ice/H_2 also pressurized to 60 MPa. Right – Raman vibron spectra of all highlighted experiments (apart from 'tuning' sample) of TBPB semi-clathrate. H_2 vibron peaks at 4130 and 4136, are very similar to the H_2 peaks of H_2 in the small cages of the THF binary hydrate, therefore confirming enclathration of H_2 in each case.

3. First Microsecond-Scale Molecular Simulations of Hydrate Nucleation & Growth *(Walsh et al., Science, 2009; Walsh et al., PNAS, in review, 2011)*

We performed the first microsecond-scale computer simulations of the nucleation of a sI clathrate hydrate and discovered for the first time the pathways to hydrate nucleation and growth (Walsh et al., Science, 2009). Figure 6 shows snapshots of the progression from the initial clustering of water and methane molecules to a fluctuating network that grows to a clathrate hydrate structure at the end. These results were the first to provide a molecular level description of a hydrate nucleation process.

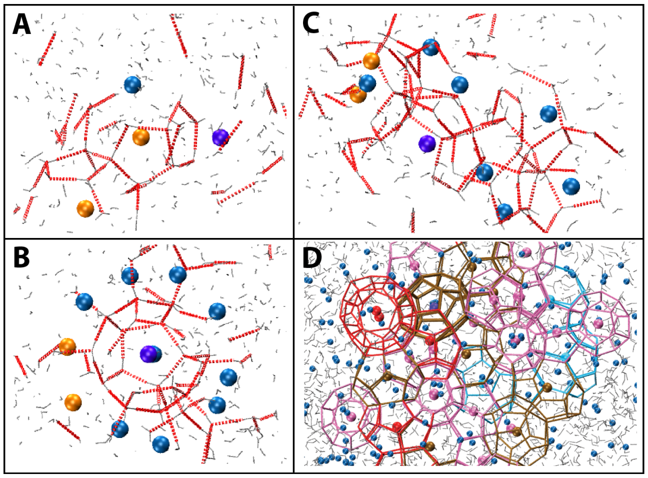


Figure 6. Fluctuating nature of the first cages involved in clathrate hydrate nucleation. The sequence in the panel shows the evolution from the initial clustering of water and methane molecules (A) to a crystalline-like state with sI and sII domains (D).

We have further investigated in 2010 the detailed mechanisms of hydrate nucleation and growth. In these investigations we have identified from microsecond-scale molecular dynamics simulations, for the first time, the most important cages in sI clathrate hydrate nucleation. We have discovered that there are seven dominant cages (not all present in the thermodynamically stable clathrate hydrate state) which are common to two different clathrate hydrate systems (methane and carbon dioxide clathrate hydrates). The interesting aspect here is that despite the two guest molecules having very different electronic and molecular structures, as well as different occupancies, with the quadrupolar CO_2 having a preference for large cages, the nucleation pathways are surprisingly similar. Furthermore, it was found, as demonstrated in Figure 7 that simple transitions between these dominant cages are made via water pair insertions and rotations. This new discovery can provide important new insight into the structure-property relations of clathrate hydrates and may help to explain the predominant metastability and ease of structural transitions observed in many clathrate systems (Walsh et al., PNAS, under review).

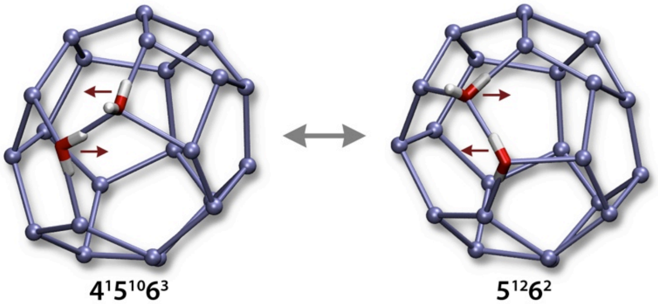


Figure 7: Example of how cage transition can happen with the simple re-arrangement of a couple of water molecules.

Conclusions

In summary, there are a number of important scientific discoveries that have been made from these studies that can be applied to future systems, and coupled with the proposed future directions on synthesis-structure-property relation investigations, the outcomes have potential key implications in all energy applications of clathrate hydrates. It is apparent that the tuning effect for binary clathrates has real potential and most likely holds the key to meeting the DOE 2015 H_2 storage target, especially since the technique can be applied to a cross/hybrid system. For binary clathrate hydrates our studies also reveal that the H_2 capacity can be very much dependent on the formation pressure, as well as the synthesis pathway/method. The ability of the H_2 molecules to occupy the large cages is strongly dependent on the initial driving force. Interestingly, neither the promoter concentration nor the formation pressure has as significant an impact on the H_2 capacity for the semi-clathrate structure, as it does for the binary clathrate hydrate system. Only when the TBPB concentration is reduced to the point where it inhibits hydrate growth does the concentration play a significant role. Additionally, the formation pathway does not appear to play a major role in the H_2 capacity for the semi-clathrate material. This is likely due to the inherent structural nature of the semi-clathrate, whereby the guest-host strong coupling/H-bonding is required to stabilize the semi-clathrate framework. For a high capacity, weaker guest-host coupled system such as the binary THF/acetone clathrate materials, these factors (synthetic pathway, formation pressure/driving force) appear to play a much greater role in the structure-stability phenomena. Molecular simulations reveal the molecular pathways towards formation/synthesis of clathrate hydrate systems, in which there are seven dominant cage structures which are formed before the stable crystal structure evolves. This has implications to the structure-stability-synthesis pathways for clathrate materials, and controlling/simulating these different evolving cage types may lead to new and more stable clathrate structures and materials.

Future Directions for Proposed Project Renewal:

The focus of the previous work (summarized above) was to discover novel chemical-clathrate hybrids and molecular clathrate materials offering a promising and innovative technology for the storage of H_2. As evidenced from the breakthrough discoveries and high impact publications summarized above, the project has made excellent progress in advancing our understanding of clathrate hydrates for energy storage. The proposed renewal exploits our current knowledge to build the fundamental science of key processes controlling the synthesis and structures of clathrate hydrates containing H_2 and other guest molecules for energy storage. Therefore, this proposal extends the current award and expands the scope of the research focusing on the molecular level interactions between guest and host molecules in clathrate hydrates. This proposed extension of the research promises a transformative understanding of clathrate hydrate metastability that is central to the broader energy applications of clathrate hydrates.

The proposed renewal of this project will enable us to continue this work and momentum of our new science discoveries and molecular and synthetic tools to probe key questions of metastability of hydrates that are related to synthesis, structure, and composition of clathrate hydrates. The questions on metastability are pivotal in all energy applications of clathrate hydrates, including energy storage, energy transportation, and energy recovery.

References

1. *Hydrogen Clusters in Clathrate Hydrate,* Mao, W. L., Mao, H., Goncharov, A. F., Struzhkin V. V., Guo, Q., Hu, J., Shu, J., Hemley, R. J., Somayazulu, M., Zhao, Y., *Science*, **297**, 2247 – 2249 (2002)
2. *Stable Low-Pressure Hydrogen Clusters Stored in a Binary Clathrate Hydrate,* Florusse, L. J., Peters, C. J., Schoonman, J., Hester, K. C., Koh, C. A., Dec, S. F., Marsh, K. N., Sloan, E. D., *Science*, **306**, 469 – 471 (2004)
3. *Molecular Hydrogen Storage in Binary THF-H_2 Clathrate Hydrates,* Strobel, T. A., Taylor, C. J., Hester, K. C., Dec, S. F., Koh, C. A., Miller, K. T, Sloan. E. D., *JPC*, **110**, 17121 – 17125 (2006)
4. *Phase Relations and Binary Clathrate Hydrate Formation in the System H_2-THF-H_2O,* Anderson, R., Chapoy, A., Tohidi, B., *ACS*, **23**, 3440 – 3444 (2007)
5. *Molecular Hydrogen Occupancy in Binary THF-H_2 Clathrate Hydrates by High Resolution Neutron Diffraction,* Hester, K. C., Strobel, T. A., Huq, A., Schultz, A. J., Sloan, E. D., Koh, C. A., *J. Phys. Chem. B*, **110**, 14024 - 14027 (2006)
6. *Properties of the Clathrates of Hydrogen and Developments in Their Applicability for Hydrogen Storage,* Strobel, T. A., Hester, K. C., Koh, C. A., Sum, A. K., Sloan, E. D, *Chem. Phys. Lett.*, **478**, 97-109 (2009)
7. Strobel, T., *On Some Clathrates of Hydrogen*, Phd Thesis, T-6457, Colorado School of Mines, Golden CO, August (2008)
8. *Storage Capacity of Hydrogen in Tetrahydrofuran,* Hydrate*,* Ogata, K., Hashimoto, S., Sugahara, T., Moritoki, M., Sato, H., Ohgaki, K., *Chem Eng Science*, **63**, 5714 – 5718 (2008)
9. *CO2 Enclathration in Hydrates of Peralkyl-(Ammonium/Phosphonium) Salts: Stability Conditions and Dissociation Enthalpies,* Mayoufi, N., Dalmazzone, D., Furst, W., Delahaye, A., Fournaison, L., *Chem Eng Data*, **55**, 1271 – 1275 (2010)
10. *Hydrogen Sulfide Separation Using Tetra-n-butyl Ammonium Bromide Semi-clathrate (TBAB) Hydrate,* Kamata, Y., Yamakoshi, Y., Ebinuma, T., Oyama, H., Shimada, W., Narita, H., *Energy and Fuels*, **19**, 1717 – 1722 (2005)
11. *Low-Pressure Molecular Hydrogen Storage in Semi-clathrate Hydrates of Quaternary Ammonium Compounds,* Chapoy, A., Anderson, R., Tohidi, B., *JACS*, **129**, 746 - 747 (2007)
12. *Stoichiometry of Clathrates,* Dyadin, Y. A., Bondaryuk, I. V., Aladko, L. S. J., *Struct. Chem.*, **36**, 995 – 1045 (1995)
13. *Tetra-n-butylammonium Borohydride Semi-clathrate: A Hybrid Clathrate Hydrate for Hydrogen Storage,* Shin, K., Kim, Y., Strobel, T. A., Prasad, P. S. R., Sugahara, T., Lee, H., Sloan, E. D., Sum, A. K., Koh, C. A., *Phys Chem*, **113**, 6415 – 6418 (2009)
14. *Hydrogen Storage in Semiclathrate Hydrates of Tetrabutyl Ammonium Chloride and Tetrabutyl Phosphonium Bromide* Deschamps, J., Dalmazzone, D., *Chem Eng Data*, **55**, 3395 – 3399 (2010)

15. *Large-Cage Occupancies of Hydrogen in Binary Clathrate Hydrates Dependent on Pressure and Guest Concentrations,* Sugahara, T., Haag, J. C., Prasad, P. S. R., Warntjes, A. A., Sloan, E. D., Koh, C. A.; Sum, A. K. *J. Am. Chem. Soc.*, submitted (2010)
16. *Increasing Hydrogen Storage Capacity Using Tetrahydrofuran,* Sugahara, T., Haag, J. C., Prasad, P. S. R., Warntjes, A. A., Sloan, E. D., Sum, A. K., Koh, C. A. *J. Am. Chem. Soc.*, **131**, 14616 - 14617 (2009).
17. *Calculation of Liquid Water-Hydrate-Methane Vapor Phase Equilibria from Molecular Simulations,* Jensen, L.; Thomsen, K., von Solms, N., Wierzchowski, S., Walsh, M. R., Koh, C. A., Sloan, E. D., Wu, D. T., Sum, A. K., *J. Phys. Chem. B.,* **114** (17), 5775-5782 (2010)
18. *Raman spectroscopic studies of hydrogen clathrate hydrates*, Strobel, T.A., Sloan, E.D., Koh, C.A., Journal of Chem. Phys., 130, 014506 (2009)
19. *Structural Transformations of sVI tert-Butylamine Hydrates to sII Binary Hydrates with Methane*, Prasad, P.S.R., Sugahara, T., Sum, A. K., Sloan, E. D., Koh, C. A., J. Phys. Chem. A, **113**, 11311-11315 (2009)
20. *Storage in Double Clathrates with tert-Butylamine,* Prasad, P.S.R. et al., Hydrogen J. Phys. Chem. A Letters, 113, 6540-6543 (2009)
21. *Microsecond Simulations of Spontaneous Methane Hydrate Nucleation and Growth, Science,* Walsh, M.R. Koh, C. A., Sloan, E. D., Sum, A. K., Wu, D. T., **326,** 1095-1098, 2009

Progress Report (9/1/2005 - 8/31/2008)

DOE Award Number: DE-FG02-05ER46242
Title of Award: "Molecular Hydrogen Storage in Novel Binary Clathrate
Hydrates at Near-Ambient Temperatures and Pressures"
Principal Investigator: E. Dendy Sloan, Co-PIs: Carolyn A. Koh, Steven F. Dec, Kelly Miller

Summary Statement of Key Accomplishments of the Project

Excellent progress has been accomplished on this research project to-date. We have demonstrated for the first time that hydrogen can be stored within the lattice of sH clathrate hydrates and semi-clathrate hydrates. A wide range of promoter molecules have been successfully shown to facilitate this storage. Spectroscopic, diffraction, and gas analysis methods have been used to confirm the storage capacity and structures of these new materials and resolve for the first time a number of scientific uncertainties in the literature. We have developed a new path forward which includes the investigation of other types of clathrate and inclusion-compound based structures as well as a novel hybrid technology that utilizes hydrogen storage from both guest and host. An understanding of the occupancy and orientation of hydrogen in the host water lattice will be key to the future development of these hydrate materials. This work demonstrates the potential of storing hydrogen in other inclusion compound materials with potentially even greater hydrogen storage capabilities.

Introduction

Clathrate hydrates are molecular inclusion compound that trap small guest molecules in hydrogen-bonded water cavities.[1] Historically, hydrogen was thought to be too small of a molecule to contribute to the stability of these structures.[2] In 2002, Mao et al.[3] confirmed the formation of structure two (sII) hydrogen clathrate hydrate. It is now generally believed that the small cavities of this clathrate contain one hydrogen molecule, and the large cavities may contain up to four hydrogen molecules, yielding a hydrogen storage capacity slightly under 4wt%.[4]

The molecular storage of hydrogen in clathrate form presents several advantages over conventional hydrogen storage materials. For pure H_2 hydrate the storage material is pure water. When hydrogen is released from the hydrate the only byproduct is benign and reusable. Also, the formation kinetics have been demonstrated to be very rapid;[5] complete conversion of H_2 clathrate from powdered ice takes place over a period of minutes. Additionally, hydrogen is stored in molecular form meaning that no chemical reaction is needed for release and the binding energy is low so that heat generation will not be problematic. The primary disadvantage for using pure hydrogen hydrate as a hydrogen storage material is the pressure required for formation (200 MPa at ~273K).[6]

In 2004, in collaboration with the Technical University of Delft, we demonstrated that the formation pressure of pure H_2 clathrate can be reduced by almost two orders of magnitude (5 MPa at 280 K), with the addition of the stabilizing additive tetrahydrofuran (THF).[7] Clearly, bringing the formation conditions of hydrogen hydrate closer to ambient conditions is an initial step towards the realization of hydrates as hydrogen storage materials.

The general focus of this work has been to explore the feasibility of binary hydrates as hydrogen storage materials in terms of hydrogen capacity and stability while obtaining a fundamental understanding of the molecular level behavior of these crystalline compounds. We have performed a detailed study on the THF/H_2 binary clathrate system and determined the maximum hydrogen content is about 1.0wt%. This hydrogen content is independent of THF composition. We have also successfully synthesized various other novel clathrate structures including: sII Cyclohexanone/H_2 hydrate, tetrabutylammonium bromide/H_2 semi-clathrate and various binary sH hydrogen hydrates. We have concluded that hydrogen is capable of forming many types of clathrate structures; this is in stark contrast to the original reports[2] that hydrogen cannot contribute to the stability of these compounds. Continued research into new clathrate compounds could lead to high capacity hydrogen storage materials. Additionally, we have performed various Raman spectroscopic studies to elucidate the molecular behavior of confined hydrogen. Finally, we have tested the hypothesis of using chemical additives to improve the thermodynamic stability of these structures. From the course of this work we have developed a new path forward which includes the investigation of other types of clathrate and inclusion-compound based structures as well as a novel hybrid technology that utilizes hydrogen storage from both guest and host.

THF/H_2 Binary Clathrate

Several techniques have been employed to determine the hydrogen storage capacity of the stoichiometric THF/H_2 binary hydrate (5.6 mol % THF). Gas release measurements, ^{1}H MAS NMR spectroscopy, and high resolution neutron diffraction were utilized to determine the hydrogen content of these materials. The experimental results showed that stoichiometric tetrahydrofuran (THF) hydrate stores up to about 1.0 wt% hydrogen.[8,9] The storage capacity of hydrogen increased with increasing pressure and was modeled well with a single adsorption Langmuir isotherm. Using high resolution neutron diffraction (at Argonne National Laboratory), molecular hydrogen was found to only singly occupy the sII small cavity. The occupancy in the small dodecahedral (5^{12}) cavity is an important parameter to assess whether these materials will be viable hydrogen storage media. Hydrate structures which enable multiple occupancy of hydrogen will facilitate increases in the stored hydrogen density. An understanding of the occupancy and orientation of hydrogen in the host water lattice will be key to the future development of these binary hydrate materials.

It was suggested be Lee et al.[10] that at low concentrations of THF, some of the large cages could become quadruply occupied by hydrogen (forming a non-stoichiometric hydrate), with hydrogen stored at around 4 wt%. In the present work, hydrates from non-stoichiometric THF/water compositions (below 5.6 to 0.5 mol %) were formed and gas release experiments were performed to investigate the possible manipulation of the large cage occupancy. As the THF concentration was decreased, there was no detectable change in storage capacity with a constant formation pressure of 13.8 MPa.[9] These results together with the neutron data, indicate that, contrary to previous reports (Lee et al.[10]), THF remains the favorable guest for the large cage.

CHONE/H_2 Binary Clathrate

Cyclohexanone is a known sII hydrate former.[11] However, like other large sII formers (e.g. cyclohexane or benzene), a second guest molecule is required to stabilize the structure.[12] No pure cyclohexanone hydrate is currently known. Using neutron powder diffraction (at Argonne National Laboratory), we have demonstrated that hydrogen acts like a well-behaved hydrate former. That is, hydrogen can stabilize the larger sII lattice in cooperation with cyclohexanone.[13] The ability of hydrogen to stabilize the larger hydrate lattice has implications for the formation of other hydrate structures with hydrogen, where a second guest molecule is needed for stability, for example sH which has greater hydrogen storage potential (see below).

TBAB/H_2 Semi-clathrate

Tetra-n-butylammonium bromide (TBAB) forms a semi-clathrate with water at atmospheric pressure. Gas release experiments were performed to investigate if H_2 molecules can be stored within the empty cavities of the semi-clathrate framework. We have shown for the first time that hydrogen molecules can be encapsulated inside the small cavities of TBAB hydrate.[14] This finding indicates that hydrogen storage in clathrate compounds is not limited to the classical clathrate hydrate structures, but can be applied to a wider variety of water-based host complexes.

Binary sH Clathrates

For the first time, in collaboration with colleagues at the Technical University of Delft (The Netherlands), we have determined that hydrogen molecules may be contained within the small water cavities of a binary sH clathrate hydrate with promoter molecules suitable for stabilizing the large eicosahedral cavity. Phase equilibrium, X-ray diffraction, and Raman spectroscopic measurements have been used to confirm molecular hydrogen storage in the binary sH clathrate hydrate. At 274 K the sH 1,1-dimethylcyclohexane+H_2 hydrate requires only 25% of the pressure needed for the simple sII hydrogen hydrate, and the potential increase in hydrogen storage could be more than 40% when compared with binary sII hydrates. This work demonstrates the stabilization of hydrogen in a hydrate structure previously unknown for encapsulating molecular hydrogen, indicating the potential for other inclusion compound materials with even greater hydrogen storage capabilities.

Raman Studies of H_2 Clathrates

Limited spectroscopic studies have been performed previously on clathrate materials containing hydrogen and significant knowledge gaps remain on the dynamic behavior of confined hydrogen molecules, as well as the interactions between the guest and host. In order to gain a better fundamental understanding of this behavior, a novel high pressure and low temperature apparatus has been constructed for the application of Raman spectroscopic measurements. Raman spectra of different hydrate phases containing hydrogen have been investigated in order to determine the cavity specific contributions to these spectra, and to probe the fundamental interactions of enclathrated hydrogen molecules. This new information can aid in understanding the structure-stability relationship of hydrated hydrogen compounds and their development.

Raman spectra for several hydrogen hydrate systems (sI, sII, sH) were successfully obtained over a range of temperatures and pressures. Hydrogen molecules within all of the structures vibrate at a lower fundamental frequency and show increased peak width when compared with the free fluid phase. This decreased vibrational frequency and peak broadening is currently being used to describe the fundamental interactions between hydrogen and the host water lattice. Additionally, we have assigned the vibrational frequencies for hydrogen molecules in the different types of water cavities for binary hydrates, as well the contributions to the Raman spectrum of pure sII hydrogen hydrate from hydrogen molecules in both the small and large cavities.[14]

Thermodynamic Promotion

Hydrotrope molecules were previously reported to promote gas hydrate thermodynamics (Gnanendran et al.[15]), by shifting the three phase (H-L_w-V) equilibrium curve to higher T/lower P. Motivated by the potential applicability of this phenomenon to pure hydrogen hydrates, the effect of p-TSA on the three phase (H-L_w-V) equilibria of three different gas hydrate forming systems was investigated (CH_4-water-p-TSA, CH_4+C_2H_6-water-p-TSA and a natural gas mixture-water-p-TSA). The equilibrium conditions (H-L_w-V) of these gas hydrate systems were obtained using an isochoric temperature cycling method at different p-TSA concentrations. However, no effect was observed on the hydrate phase equilibria with hydrotrope concentrations in the range of 2000-5000 ppm.[16] Furthermore, at higher concentrations (up to 138,000 ppm), an inhibition effect on the CH_4 hydrate stability was measured. Extremely high heating rates were most likely the cause of the shifted equilibrium curves reported in Gnanendran et al.[15]

Hybrid Chemical-Clathrate Technology

For the first time we have demonstrated a proof-of-principle technology that utilizes hydrogen storage from both guest and host (Strobel et al., 2007, in preparation) Preliminary results indicate the formation of a new clathrate structure with hydroquinone and hydrogen. In this scenario, the hydroquinone plays the role of the host in the clathrate while molecular hydrogen is the guest. Additionally, we have demonstrated that after molecular hydrogen is released from the clathrate, we can chemically dehydrogenate the hydroquinone host crystal to produce additional hydrogen gas. Hydrogen storage under this scenario poses many advantages as storage is provided form two independent sources within the same material.

Future Plans

Currently, no technology can meet all of the 2015 DOE's goals for hydrogen storage materials and it is accepted that new materials spanning broad disciplines must be developed. Recently, we have hypothesized novel hybrid hydrogen storage materials that utilize storage in both chemical and molecular form. Storage under this scenario could potentially increase the overall capacity greatly. Preliminary results suggest the feasibility of this scenario for a model system.

One of the most significant conclusions resulting from this study is that hydrogen is capable of forming numerous types of clathrate structures and is not limited to the sII hydrate lattice. Due to the large number of known clathrate structures that have not yet been investigated, we propose to investigate the hydrogen storage potential of other types of clathrate materials. These aspects will be discussed in greater detail in the proposal section.

Conclusions

The hydrogen storage potential of several clathrate materials has been investigated through macro and microscopic means. We have performed a detailed study on the THF/H_2 binary clathrate system and determined the maximum hydrogen content is about 1.0wt% with this hydrogen content being independent of THF composition. We have also successfully synthesized various other novel clathrate structures including: sII Cyclohexanone/H_2 hydrate, tetrabutylammonium bromide/H_2 semi-clathrate and various binary sH hydrogen hydrates under a range of pressure and temperature conditions. The formation of these clathrate structures with hydrogen provides evidence that hydrogen is capable of being contained within a wide array of molecular compounds and that analogies can be drawn between hydrogen clathrates and clathrates with more common guests (e.g. methane). Continued research into new clathrate compounds could lead to high capacity hydrogen storage materials. Additionally, we have performed various Raman spectroscopic studies to elucidate the molecular behavior of confined hydrogen. We have identified unique spectroscopic signals for hydrogen in various clathrate environments. This spectroscopic information is being used to describe the fundamental interactions between hydrogen and the water host lattice. Finally, we have tested the hypothesis of using hydrotrope chemical additives to improve the thermodynamic stability of these structures and determined that this approach is not feasible for clathrate materials. From the course of this work we have developed a new and promising path forward which includes the investigation of other types of clathrate and inclusion-compound based structures as well as a novel hybrid technology that utilizes hydrogen storage from both guest and host.

References

1. Sloan, E. D. & Koh, C. A. *Clathrate Hydrates of Natural Gases, Third Edition* (Taylor & Francis - CRC Press, Boca Raton, 2008).
2. Holder, G. D. et al. Formation of Clathrate Hydrates in Hydrogen-Rich Gases. *Ind. Eng. Chem. Proc. Des. Dev.* 22, 170 (1983).
3. Mao, W. L. et al. Hydrogen clusters in clathrate hydrate. *Science* 297, 2247 (2002).
4. Lokshin, K. A. et al. Structure and Dynamics of Hydrogen Molecules in the Novel Clathrate Hydrate by High Pressure Neutron Diffraction. *Phys. Rev. Lett.* 93, 125503 (2004).
5. Lokshin, K. A. & Zhao, Y. Fast Synthesis and Phase Diagram of Hydrogen Clathrate Hydrate. *Appl. Phys. Lett.* 88, 131909 (2006).
6. Dyadin, Y. et al. Clathrate hydrates of hydrogen and neon. *Mendeleev Commun.* 5, 209 (1999).
7. Florusse, L. J. et al. Stable Low-Pressure Hydrogen Clusters Stored in a Binary Clathrate Hydrate. *Science* 306, 469 (2004).

8. Hester, K. C., Strobel, T. A., Sloan, E. D. & Koh, C. A. Molecular Hydrogen Occupancy in Binary THF-H2 Clathrate Hydrates by High Resolution Neutron Diffraction. *J. Phys. Chem. B* 110, 14024 (2006).
9. Strobel, T. A. et al. Molecular Hydrogen Storage in Binary THF-H2 Clathrate Hydrates. *J. Phys. Chem. B* 110, 17121 (2006).
10. Lee, H. et al. Tuning Clathrate Hydrates for Hydrogen Storage. *Nature* 434, 743 (2005).
11. Ripmeester, J. A., Tse, J. S., Ratcliffe, C. I. & Powell, B. M. A New Clathrate Hydrate Stucture. *Nature* 325, 135 (1987).
12. Ripmeester, J. A. & Ratcliffe, C. I. 129Xe NMR Studies of Clathrate Hydrates: New Guests for Structure IIand Structure H. *J. Phys. Chem.* 94, 8773 (1990).
13. Strobel, T. A., Hester, K. C., Sloan, E. D. & Koh, C. A. A Hydrogen Clathrate Hydrate with Cyclohexanone: Structure and Stability. *J. Am. Chem. Soc.* 129, 9544-9545 (2007).
14. Strobel, T. A., Koh, C. A. & Sloan, E. D. Hydrogen Storage Properties of Clathrate Hydrate Materials. *Fluid Phase Equilib.* 261, 382 (2007).
15. Gnanendran, N. & Amin, R. Equilibrium Hydrate Formation Conditions for Hydrotrope-Water-Natural Gas Systems. *Fluid Phase Equilib.* 221, 175 (2004).
16. Rovetto, L. J., Strobel, T. A., Koh, C. A. & Sloan, E. D. Is Gas Hydrate Formation Thermodynamically Promoted by Hydrotrope Molecules. *Fluid Phase Equilib.* 247, 84 (2006).

Publications Acknowledging the Grant or Contract 9/2005 – 8/2014

1. Molecular Hydrogen Storage in Binary THF-H_2 Clathrate Hydrates, Strobel, T.A.; Taylor, C.J; Hester, K.C.; Dec, S.F.; Koh, C.A.; Miller, K.T.; Sloan, E.D., *J. Phys. Chem. B* (2006), **110**, 17121-17125.

2. Molecular Hydrogen Occupancy in Binary THF-H2 Clathrate Hydrates by High Resolution Neutron Diffraction, Hester, K. C.; Strobel, T.A.; Sloan, E.D.; Huq, A.; Schultz, A.J.; Koh, C.A. J. Phys. Chem. B, (2006), **110**, 14024-14027.

3. Is Gas Hydrate Formation Thermodynamically Promoted by Hydrotrope Molecules, Rovetto, L.J.; Strobel, T.A.; Koh, C.A.; Sloan, E.D., *Fluid Phase Equilibria* (2006), **247**, 84-89.

4. A Hydrogen Clathrate Hydrate with Cyclohexanone: Structure and Stability, Strobel, T.A.; Hester, K.C.; Sloan, E.D.; Koh, C.A., *J. Am. Chem. Soc.* (2007), **129**, 9544-9545.

5. Water Cavities of Structure H Clathrate Hydrate Stabilized by Molecular Hydrogen, Strobel, T.A.; Koh, C.A.; Sloan, E.D., *J. Phys. Chem. B* (2008), **112**, 1885-1887.

6. Hydrogen Storage Properties of Clathrate Hydrate Materials, Strobel, T.A.; Koh, C.A.; Sloan, E.D., *Fluid Phase Equilibria* (2007), **261**, 382-389.

7. Natural Gas Hydrates: Recent Advances and Challenges in Energy and Environmental Applications, Koh, C.A.; Sloan, E.D. *AIChE J*. (2007), **53**, 1636-1643.

8. Chemical-Clathrate Hybrid Hydrogen Storage: Storage in Both Guest and Host, Strobel, T.A., Kim, Y.; Andrews, G.S.; Ferrell, J.R.; Koh, C.A.; Herring, A.M.; Sloan, E.D., *J. Am. Chem. Soc.* (2008), **130**, 14975.

9. Strobel, T., On Some Clathrates of Hydrogen, PhD Thesis, T-6457, Colorado School of Mines, Golden CO, August 2008.

10. Microsecond Simulations of Spontaneous Methane Hydrate Nucleation and Growth, Walsh, M.R.; Koh, C.A.; Sloan, E.D.; Sum, A.K.; Wu, D.T. *Science* (2009), **326**, 1095-1098.

11. Raman Spectroscopic Studies of Hydrogen Clathrate Hydrates, Strobel, T.A., Sloan, E.D., Koh, C.A., *J. Chem. Phys.* (2009), **130**, 014506.

12. Increasing Hydrogen Storage Capacity Using Tetrahydrofuran, Sugahara, T.; Haag, J.C.; Prasad, P.S.R.; Warntjes, A.A.; Sloan, E.D.; Sum, A.K.; Koh, C.A., *J. Am. Chem. Soc.,* (2009), **131**, 14616-14617.

13. Properties of the Clathrates of Hydrogen and Developments in their Applicability for Hydrogen Storage, Strobel, T.A.; Hester, K.C.; Koh, C.A.; Sum, A.K.; Sloan, E.D., *Chem. Phys. Lett.* (2009), **478**, 97-109.

14. Thermodynamic Predictions of Various Tetrahydrofuran and Hydrogen Clathrate Hydrates, Strobel, T.A.; Koh, C.A.; Sloan, E.D. *Fluid Phase Equilibria* (2009), **280**, 61-67.

15. Tetra-n-butylammonium Borohydride Semiclathrate: A Hybrid Material for Hydrogen Storage, Shin, K.; Kim, Y.; Strobel, T.A.; Prasad, P.S.R.; Sugahara, T.; Lee, H.; Sloan, E.D.; Sum, A.K.; Koh, C.A., *J. Phys. Chem. A* (2009), **113**, 6415 – 6418.

16. Koh, C.A., Sum, A.K., Sloan, E.D., Gas Hydrates: Unlocking the energy from icy cages, Focused Review, *J. Appl. Phys*. (2009), **106**, 061101.

17. Sum, A. K.; Koh, C. A.; Sloan, E. D., Clathrate Hydrates: From Laboratory Science to Engineering Practice, *Industrial & Engineering Chemistry Research* (2009), **48** (16), 7457-7465.

18. The Cages, Dynamics, and Structuring of Incipient Methane Clathrate Hydrates, M. R. Walsh, J. D. Rainey, P. G. Lafond, D.-H. Park, G. T. Beckham, M. D. Jones, K.-H. Lee, C. A. Koh, E. D. Sloan, D. T. Wu, A. K. Sum, *Phys. Chem. Chem. Phys.* (2011), **13**, 19951-19959.

19. Methane Hydrate Nucleation Rates from Molecular Dynamics Simulations: Effects of Aqueous Methane Concentration, Interfacial Curvature, and System Size, M. R. Walsh, G. T. Beckham, C. A. Koh, E. D. Sloan, D. T. Wu, A. K. Sum, *J. Phys. Chem.* (2011) **115**, 21241-21248.

20. Rapid Hydrogen Hydrate Growth from Non-Stoichiometric Tuning Mixtures During Liquid Nitrogen Quenching, R. G. Grim, P. B. Kerkar, E. D. Sloan, C. A. Koh, A. K. Sum, *J. Chem. Phys.* (2012) **136**, 234504.

21. Synthesis and Characterization of sI Clathrates Containing Hydrogen, R. G. Grim, P. B. Kerkar, M. Shebowich, M. Arias, E. D. Sloan, C. A. Koh, A. K. Sum, *J. Phys. Chem. C.* (2012), **116**, 557-563.

22. Micromechanical Cohesion Force Measurements to Determine Cyclopentane Hydrate Interfacial Properties, Z.A. Aman, S. Joshi, E.D. Sloan, A.K. Sum, C.A. Koh, *J. Colloid Interface Sci.*, (2012), **376**, 283-288.

23. Lowering of Clathrate Hydrate Cohesive Forces by Surface Active Carboxylic Acids," Z. M. Aman, E. D. Sloan, A. K. Sum, and C. A. Koh, *Energy & Fuels* (2012), **26**, 5102.

24. Surfactant Adsorption and Interfacial Tension Investigations on Cyclopentane Hydrate, Z. M. Aman, K. Olcott, K. Pfeiffer, E. D. Sloan, A. K. Sum, C. A. Koh, *Langmuir* (2013), **29**, 2676-2682.

25. Adhesion Force between Cyclopentane Hydrate and Mineral Surfaces, Z. A. Aman, W. J. Leith, G. A. Grasso, E. D. Sloan, A. K. Sum, C. A. Koh, *Langmuir* (2013), **29**, 15551-15557.

26. Measurements of Cohesion Hysteresis Between Cyclopentane Hydrates in Liquid Cyclopentane", N. Maeda, Z. M. Aman, K. A. Kozielski, C. A. Koh, E. D. Sloan, A. K. Sum, *Energy & Fuels* (2013), **27**, 5168-5174.

27. Investigating the Thermodynamic Stabilities of Hydrogen and Methane Binary Gas Hydrates", Y. Matsumoto, R. G. Grim, M. N. Khan, T. Sugahara, K. Ohgaki, E. D. Sloan, C. A. Koh, A. K. Sum, *J. Phys. Chem. C.* (2014), **118**, 3783-3788.

28. Observation of Metastable Interstitial Molecular Hydrogen in Clathrate Hydrates", R. G. Grim, A. K. Soper, W. A. Kockelmann, D. A. Keen, C. A. Koh, A. K. Sum, *Angewandte Chemie* (2014), **53**, 10710-10713.

29. Quantitative Measurement of CH4 Production from Hydrates with the Injection of Liquid CO2, B. R. Lee, C. A. Koh, and A. K. Sum, *Physical Chemistry Chemical Physics* (2014) **16**, 14922-14927.

List of Personnel Working on the Project

Name	Title	2005-2006	2006-2007	2007-2008	2008-2009	2009-2010	2010-2011	2011-2012	2012-2013	2013-2014
Carolyn Koh (PI: 9/2011-8/2014)	Academic Faculty				Jun'08, 100% - 22 days	Jan'10, 100% - 5 days	May-Jun'11, 100% - 34 days	July'11, 100% - 21 day	June'13 100% - 20 day	May'14 80%-12 days
Steven Dec	Academic Faculty	Feb, Mar'06, 100%	Jul, Aug'06, 100%							
E. Dendy Sloan (PI: 9/2005-8/2011)	Academic Faculty				May'09, 67% 10 days					
Amadeu Sum	Academic Faculty					Oct'09,Jan-Feb'10, 100% - 5 days				Aug'14 100%-12 days
Kelly Miller	Research Faculty	Jan-Jun'06 100%	Jul-Dec'06, May-June' 07 100%	Jul-Aug'07 100%						
Laura Rovetto	Research Faculty (Postdoc)	Jan-Jun'06 100%	Jul'06-Jun'07 100%	Jul-Sept'07 100%						
Andrews	Research Faculty (Visiting graduate student)			Sept-Nov'07, 100%						
Ohno	Research Faculty (Postdoc)			Sept'07-May'08, 100%						
Pinnelli Prasad	Research Faculty (Postdoc)				Sept'08, 70%					
Sugahara	Research Faculty (Postdoc)				Dec'08-Jun'09, 100%	Jul-Nov'10, 100%				
Taghikhani	Research Faculty (Postdoc)				Nov'08-Jun'09, 100%					
Yoon	Research Faculty (Postdoc)					Yoon - Dec'09-May'10 100%				
Haag	Research Faculty (Hourly)					June'10, Hourly	July'10, Hourly			
Kerkar	Research Faculty (Postdoc)						Nov'10-Jun'11, 100%	Jul-Aug'12, 100%		
Braniff	Research Faculty (Visiting student)							Aug'11, 100%		
Matsumoto	Research Faculty (Visiting student)								Jul'12-Jan'13, 100%	
Adhangale	Research Faculty (Postdoc)								Dec '12 - June'13, 100%	July 13-Nov13, 100%
Lee	Research Faculty (Postdoc)								Jul '12 - Jun '13. 65%	Jul13 - Feb14, 70%
Cha	Research Faculty (Postdoc)									Sept'13 - Apr'14, 50%
T. Strobel	GRA Salary	May-Jun'06, 100%	100%	Jul'07 - Apr'08, 100%						
Joshi	GRA Salary			Sept-Dec'07 100%						
Lachance	GRA Salary			Jan-Feb'08 100%						
Davies	GRA Salary			Jan-Apr'08 100%						
Guariguata	GRA Salary			Jan-Apr'08 100%						
Nicholas	GRA Salary			Jan-Apr'08 100%						
Pascall	GRA Salary				Sept'08-Apr'09, 100%	Sept'09-Apr'10, 100%				
Mulligan	GRA Salary				Sept'08-Jun'09, 100%	Jul-Sept'10, 100%				
Walsh	GRA Salary				Sept'08-Jun'09, 100%	100%	100%	Jul-Aug'11, 100%		
LaFond	GRA Salary					Jan-Jun'10, 100%	Jul-Nov'10, 100%			
Robert Grim	GRA Salary						May-Jun'11, 100%	Jul-Aug'11, 100%	100%	100%
Jones	GRA Salary						Jan-Jun'11, 100%	Jul-Aug'11, 100%	Jul-Aug'13, 100%	
Wilson	GRA Salary									Jan-Jun'14, 100%
George	Student Hourly			5-10 hrs/week						
Kim	Student Hourly			5-10 hrs/week						
Gilmer	Student Hourly					5-10 hrs/week				
Haag	Student Hourly					5-10 hrs/week				
Maul	Student Hourly					5-10 hrs/week				
Weisgerber	Student Hourly					5-10 hrs/week	5-10 hrs/week			
DiFulvio	Student Hourly					5-10 hrs/week	5-10 hrs/week			
McNair	Student Hourly									5-10 hrs/week