Raman Spectroscopic Studies of Clathrate Hydrate Formation in the Presence of Hydrophobized Particles

Huijuan Li¹, Paul Stanwix², Zachary Aman², Michael Johns², Eric May², and Liguang Wang^{1,*}

¹ *School of Chemical Engineering, The University of Queensland, Brisbane, Australia*

² *School of Mechanical and Chemical Engineering, The University of Western Australia, Perth, Australia*

ABSTRACT

In the present work, Raman spectroscopy was used to study the structure of water molecules in the vicinity of glass particles with different hydrophobicity, immersed in water and in tetrahydrofuran and cyclopentane hydrates. The glass particle surfaces were either clean (hydrophilic), or coated with *N,N*-dimethyl-*N*-octadecyl-3-aminopropyl trimethoxysilyl chloride (partially hydrophobic), or coated with octadecyltrichlorosilane (hydrophobic). The Raman spectra indicate that, prior to nucleation, water molecules in the vicinity of hydrophobic surfaces are more ice-like ordered than those in the bulk liquid or near either hydrophilic or partially-hydrophobic surfaces. Furthermore, the degree of hydrogen-bond ordering of water observed prior to hydrate nucleation, as measured by the ratio of the inter- and intra-molecular Raman OH bands, was found to have an inverse relationship with the mean induction time for hydrate formation. Following hydration formation, no significant difference in the water molecule structure was observed in the hydrate phase based on their Raman OH bands, irrespective of surface hydrophobicity. These observations made with Raman spectroscopy provide the foundations for a quantitative link between hydrate nucleation promotion and water-ordering

near solid surfaces, which could enable direct comparisons with results from corresponding molecular dynamics simulations.

Key words: Raman Spectroscopy, Clathrate Hydrate, Hydrophobized Surface, Water Structure, OH Stretching Mode

INTRODUCTION

Clathrate hydrates are nonstoichiometric ice-like solid compounds in which small guest molecules are enclathrated in water nanocages, the cavities of hydrogen-bonded host water molecules¹. In addition to the flow assurance issues caused by hydrate-induced blockages in oil/gas pipelines, natural gas hydrates have important applications in the areas of energy production and gas storage, transportation, and separation². While the thermodynamics of gas hydrates is reasonably well understood, there is still a significant need to improve the understanding of hydrate formation (nucleation and growth). In particular, many details of the nucleation process remain unclear because this process is stochastic both in terms of when it occurs (for a given driving force), and the pathway by which it occurs^{3,4}.

In recent years, molecular dynamics (MD) simulations⁴⁻⁷ have provided insights into hydrate nucleation, elucidating how the molecules establish local order and the pathways by which that local order becomes long-range. These insights reveal that the complexity of hydrate nucleation usually goes beyond theories such as the labile cluster hypothesis⁸ and the local structuring hypothesis⁹ that emphasise a particular mechanism by which it occurs.⁴ For several years, the limited resolution of nucleation experiments meant that no definitive evidence for one theory over the other could be

found.⁴ However, both of these theories under-emphasize the importance of the interactions between the guest and water molecules in the construction of partial cages that has been revealed through more recent MD simulations. These led to a sequence of more recent nucleation theories including the cage adsorption hypothesis¹⁰, the blob mechanism¹¹ and the templating mechanism¹² which are not mutually exclusive. Walsh and co-workers^{4,13} have summarized these mechanisms as follows:

- i) Adsorption: dissolved guest molecules adsorb from the solution onto planar hydrogen bonded water faces, and help stabilise them in against fluctuations.
- ii) Cooperation: the hydrophobic adsorbed guest encourage the arrangement of other stabilised water planes into cage-like structures so that as full, space-filling cages form, more adsorption sites become available for other guest molecules still in solution.
- iii) Dynamic Cages: a range of cages are formed, many of which are only temporarily stable, and these transition into a subset of stable cages usually via the rearrangement of pairs of water molecules.
- iv) Templating and Annealing: a crystalline phase with long range order then emerges from these dynamic cages which provide a template for growth and/or through the annealing of amorphous regions within the solid as cages continue to convert into their most stable forms.

These mechanisms are called the AC/DC-T&A mechanisms. Further understanding about the hydrate nucleation mechanism has been more recently advanced by Barnes et al.^{5,6}, who conducted over 180 MD simulations lasting 3 μ s or longer and identified an order parameter based on mutually coordinated guests (MCG). This MCG order parameter can serve as a reaction coordinate or metric

that can quantify progress through the various stages in the nucleation mechanism. This MCG parameter is essentially a measure of the extent to which guest molecules adsorbed onto hydrogen-bonded planar cage faces are coordinated with guest molecules adsorbed onto other stabilised cage faces. When the MCG order parameter reaches 16 a critical nucleus is formed.⁵

The respective extents to which the templating and annealing components of the AC/DC-T&A mechanisms occur are also stochastic⁴. Zhang et al.³ have shown that it is possible for hydrates to nucleate directly into a highly-crystalline sI phase, without any requirement for the annealing of amorphous intermediates. Furthermore, while most MD simulations focus on homogenous nucleation, hydrate formation in experiments and industrial situations will almost inevitably begin with heterogeneous nucleation, and in these cases the role of templating can be more prominent.

Experimental studies of clathrate nucleation also reflect a wide variety of pathways by which it can occur. For example, Devlin et al.¹⁴ have shown that hydrates can form from all-vapour mixtures at sufficiently large driving forces (which are comparable or greater than those used in MD simulations) via the formation of nanodroplets. Hawtin et al.¹⁵ reviewed the use of technologies such as neutron scattering,¹⁶⁻¹⁸ nuclear magnetic resonance, and X-ray tomography¹⁹. Under most circumstances, and consistent with MD results, the extent of local structure in the water phase, whether inferred or measured directly, is observed to correlate with experimental measures of the nucleation rate.

The introduction of particles with hydrophobic surfaces has been shown to promote hydrate formation.^{20, 21} Solid surfaces have long been hypothesised to structurally modify and induce order in the layers of water near the surface.²² Du et al.²³ used sum-frequency generation spectroscopy (SFG) to study the nature of water's OH bonds in the vicinity of different surfaces. In the presence of a solid

hydrophobic surface (quartz coated with OTS [octadecyltrichlorosilane], producing a layer of closely packed hydrocarbon chains), a peak at 3680 cm^{-1} was apparent in the water spectra, signifying the non-hydrogen-bonded (free OH) stretch vibration and suggesting that the hydrophobic surface produced by the OTS coating increased the extent of order in the water molecules near the solid interface. In contrast, no free OH peak was discernible near a partially-hydrophobic surface, namely quartz coated with DMOAP [*N,N*-dimethyl-*N*-octadecyl-3-aminopropyl trimethoxysilyl chloride], which produces a layer of loosely packed hydrocarbon chains. This suggested that the partially-wetted surfaces reduced the local degree of order in the water molecules. Bai et al.²⁴ conducted MD simulations involving SiO_2 surfaces with various degrees of hydrophobicity. These results indicated that the hydrophobicity of solid surfaces can change the local structure of water molecules and gas distribution near liquid-solid interfaces and that hydrate nucleation can occur more easily on relatively more hydrophobic surfaces. Li and Wang²⁵ studied experimentally the effect of clean glass particles, particles coated with DMOAP and particles coated with OTS on the formation rate of tetrahydrofuran (THF, water miscible) and cyclopentane (CP, water immiscible) hydrates. The highly hydrophobic OTS-coated glass particles were found to significantly accelerate nucleation of both THF and CP hydrates, whereas the partially hydrophobic DMOAP-coated glass particles and the hydrophilic clean glass particles promoted the formation of THF hydrates to a lesser degree, and had virtually no impact on the formation of CP hydrates. Contact mode AFM measurements showed little difference in surface roughness of clean glass surface and the OTS-coated glass surface²⁶; therefore, roughness of surface should not be considered the main contributor to promoting hydrate nucleation. However, in the previous study by Li and Wang²⁵ it was not possible to quantify the correlation between water

ordering near the various surfaces and the promotion of hydrate nucleation, and doing so was an objective of this study.

Raman spectroscopy has been widely applied to the study of hydrate structure, hydration number and cage occupancy at the molecular level.²⁷⁻²⁹ Recently, Raman spectroscopy was used to investigate the effect of surfactants on water structure at hydrate–water interfaces; the adsorption of surfactant at the water–hydrate interface was found to make water molecules more “clathrate-like” and enhanced the intrinsic enclathration rate upon hydrate formation.³⁰ For the purpose of observing changes in water structure, Raman spectroscopy can be employed because it can provide information about the intra- and inter-molecular vibrational modes of liquid water.³¹ The inter-molecular structure of water in liquid is usually described in terms of an extended hydrogen bonding network, in which each H₂O molecule can form up to four hydrogen bonds with their nearest neighbours. The relative strength of these hydrogen bonds can be inferred from the ratio of two Raman lines corresponding to the stretching of the OH group.³² The stronger these hydrogen bonds are, the more ordered the local water structure with H₂O molecules engaging in tetrahedral clustering.^{33, 34} Uchida et al.³⁵ used Raman spectroscopy to monitor the hydration structure of methane molecules in water and found, prior to clathrate formation, no evidence of changes in the water structure. However, in the presence of a stable hydrate crystal, a semistable cage-like structure was observed in the water phase around the CH₄ molecule. This cage-like structure was promoted by the molecular ordering at the crystal interface, but was also persistent into the liquid water at a distance of up to 2 mm. More recently, Braeuer et al.³⁶ demonstrated that Raman spectroscopy is applicable for understanding the development of hydrogen-bonding in the liquid water-rich phase just before the onset of gas hydrate formation.

In the present work, Raman spectroscopy was used to probe the relative strengths of hydrogen bonding and thus water structure in both liquid-phase solutions and in clathrate hydrates. The OH stretching modes were monitored in bulk water as well as near clean, DMOAP-coated and OTS-coated glass surfaces. We also conducted Raman spectroscopy of clathrate hydrates of water-miscible THF and water-immiscible CP, which have been widely used as model systems because they have the same hydrate structure (sII) with naturally-occurring hydrates and have easily accessible formation conditions (atmospheric pressure and near ambient temperature).^{37, 38} The differences in water structure near the various particle surfaces quantified with the Raman spectra measured prior to hydrate formation were then compared with the median induction times for hydrate formation measured for these systems. An asymptotic relationship between local water ordering and ease of hydrate formation was found.

EXPERIMENTAL

1. Materials

Deionized (DI) water was used for all of the experiments. The THF (99.9 wt% pure) and CP (98 wt% pure) used for hydrate formation were purchased from Sigma-Aldrich. Glass particles with diameters at $200 \pm 50 \mu\text{m}$ were purchased from Corpuscular. The information for the surface properties of glass particle type are given elsewhere.²⁵ The OTS (90 wt% pure) and DMOAP (72 wt% pure) were obtained from Sigma-Aldrich to chemically coat the particles.

2. Chemical coating of glass particles

The glass particles (SiO_2 72.5 mol%) were cleaned in a ‘Piranha’ solution ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 = 3:1$ by volume) for 20 minutes. They were then rinsed thoroughly with copious amounts of DI water and dried in oven at 100°C . OTS-coated glass particles and DMOAP-coated glass particles were prepared as described in our previous study.²⁵ The wettability of these particles was characterized by measuring the advancing water contact angle on plain glass slides with similar SiO_2 content (approx. SiO_2 73 mol%) subjected to the same coating procedure as the particles. A $10\mu\text{L}$ DI water drop was placed on a dry and horizontal glass slide. A side-view image was then taken by using a digital camera (Canon EOS 500D with Canon EF 100mm f2.8 Macro USM Lens), from which the contact angle was determined. The contact angle of DI water on the clean glass surface was $16.8^\circ \pm 1.5^\circ$. After DMOAP and OTS deposition, the contact angle for water on the coated glass surface increased to $70.0^\circ \pm 1.0^\circ$ and $100.0^\circ \pm 0.9^\circ$, respectively.

3. Hydrate Sample Preparation

To accelerate formation of THF and CP hydrate at ambient pressure, the hydrate samples were prepared from ice particles with a diameter around $1\mu\text{m}$ and produced using DI water. Hydrates were formed in four different systems simultaneously, with: i) no particles, ii) 5 g clean glass particles, iii) 5 g DMOAP-coated glass particles and iv) 5 g OTS-coated glass particles.

The hydrate formation procedure was as follows: 1) 3.8 g CP + 1.2 g ice particles or 0.95 g THF + 4.05 g ice particles (19.1 wt% THF - same loading amounts as in our previous study²⁵) were put in hydrate formation tubes; 2) the tubes were put in a refrigerator where the temperature was held above the ice point at 275 K for more than 12 hours; 3) hydrate formed from the melted ice. The formation of hydrate could be observed from the morphology of the particles and confirmed by measurements of

the Raman spectra. It is important to note that the temperature for hydrate formation was set to 273.5 K. This eliminated the possibility of ice contamination and whilst being below the equilibrium temperatures of THF hydrate (277.5 K³⁸) and CP hydrate (281.0 K³⁹). This choice of 273.5 K meant that the subcooling driving force for hydrate formation was about as large as it could be in both cases while precluding the formation of ice, although it was somewhat larger for CP hydrate (7.5 K) than for THF hydrate (4 K).

4. Hydrate Formation Measurements and Extended Analysis

Measurements of hydrate formation probability as a function of induction time were described in a previous communication of ours²⁵; however, a more detailed analysis of those data was performed in the present work using the framework developed by May et al.⁴⁰ Figure 1 shows the measured cumulative probability distribution functions (CPDF) as a function of induction time. In all of the experiments conducted, there were some trials in which formation did not occur after an induction time of 48 hours, which is why the CPDF functions do not reach unity on this time scale. No significant hydrate formation was observed over this time frame for either THF or CP hydrate formation in the bulk liquid. Similarly, no appreciable degree of formation was observed for CP hydrates on either clean or DMOAP-coated particles over 48 hours of induction time.

The four CPDF distributions shown in Figure 1 are sufficient to allow an estimate of the median induction times for each system (using a threshold probability of 0.5⁴⁰). These were 9.6 hours for THF hydrates on clean particles, 6.5 hours for THF hydrates on DMOAP-coated particles, 2 hours for THF hydrates on OTS-coated particles, and 5.6 hours for CP hydrates on OTS-coated particles.

5. Raman Analysis

Raman spectra were acquired using a Renishaw InVia Raman Microscope with a 532 nm laser excitation source. The resolution and range of the spectrometer were 0.5 cm^{-1} and 5400 cm^{-1} , respectively. In the case of hydrate measurements, small samples were transferred within 30 seconds from the refrigerator being held at 275 K to a temperature-controlled stage (Linkam THMS600) which was held at 274 K throughout the Raman measurements. For each hydrate sample the spectra was confirmed by at least 4 repeat measurements acquired from different locations on the sample. Raman spectra of the dry uncoated and coated glass particles were acquired (Figure 2), and served as reference spectra for background subtraction from the hydrate measurements taken in the presence of the corresponding particles. Analysis of the spectra acquired was performed using Renishaw WiRE 3.4 software.

Figure 3a shows an example of the microscope image corresponding to measurements taken with the laser focused on the water phase in the vicinity of the particles to probe their effect on the ordering of water molecules near the surface. Here the bright, circular areas correspond to the glass particles while the dark area is water. Measurements were performed by firstly focussing the laser beam in the region between two closely spaced particles. This approach was found to produce the most reliable measurement of surface effects; when focussing directly on the surface of the particles, it is difficult to optimise the focal point in the z-axis since the focus is less constrained than in the transverse plane. During the measurement, the exposure time was set as 10 seconds at 10% laser power (approximately 20 mW) and 10 accumulations (number of scan repetitions per measurement). The intensity maxima of the two major bands centred near 3200 cm^{-1} (I_{3200}) and 3400 cm^{-1} (I_{3400}) for the OH stretching mode were analysed to estimate the extent of the water structure ordering.^{41,42} An increase in the peak

intensity ratio (I_{3200}/I_{3400}) is an indication of hydrogen-bond ordering (or more orderly ice-like structure) in the water molecular arrangement, and a decrease in the ratio represents bond disordering.

RESULTS AND DISCUSSION

1. OH stretching mode of water

Figure 3(b) shows the Raman spectra of water in bulk and near the surface of the clean, DMOAP-coated, and OTS-coated glass particles. The Raman bands centred at ~ 3200 and ~ 3400 cm^{-1} represent water molecules that are hydrogen-bonded. Both of the protons of these water molecules are involved in hydrogen bonding, and both of the lone electron pairs are also involved in hydrogen bonding. The spectrum at ~ 3200 cm^{-1} represents the vibrations of strongly hydrogen-bonded OH-groups, which indicates an ordered arrangement of water molecules;⁴² specifically the band centred at ~ 3200 cm^{-1} is attributed to the OH mode of tetrahedrally-coordinated hydrogen-bonded water, which is normally the most intense band in the spectrum of ice. The spectrum at ~ 3400 cm^{-1} represents more weakly hydrogen-bonded OH-groups for water molecules³⁹ in an incomplete tetrahedral coordination (i.e. slightly disordered) hydrogen-bonded structure. This band at 3200 cm^{-1} is often referred to as the “ice-like” mode, whereas the band at 3400 cm^{-1} is referred to as the “liquid-like” mode.⁴³

In bulk water, the dominant mode of OH stretching was around 3400 cm^{-1} . Near clean and DMOAP-coated surfaces, the band centred at 3400 cm^{-1} was less dominant compared with bulk water; while in the vicinity of OTS-coated surface, the dominant peak shifted from 3400 cm^{-1} to 3200 cm^{-1} .

The results indicate that the water molecules are more ordered near these solid surfaces, especially the highly hydrophobic OTS-coated surface than that in bulk water.

The data in Figure 3(b) show that the ratio of the two OH stretching bands, $R_{\text{OH-W}} = I_{3200}/I_{3400}$ (which is similar to the quantity used by Burikov et al.⁴⁴), increased not only as the surface of the particles was approached, but also as the wetting characterization of those surfaces changed from hydrophilic to hydrophobic. The intensity of a Raman band depends linearly on the concentration of its related functional group; therefore, the ratio of peak intensities, $R_{\text{OH-W}}$, can be used to estimate the ratio of OH bonds in an ice-like mode (regular tetrahedral structure with strong hydrogen bonds.⁴⁵) to those in a liquid-like mode.^{46, 47} The results obtained here indicate that increasing surface hydrophobicity leads to an increase in the relative number of tetrahedrally coordinated strongly hydrogen-bonded water molecules. The results obtained in the present work with Raman spectroscopy are consistent with the results obtained in previous SFG studies, where the ordering of water molecules is enhanced near surfaces and particularly near hydrophobic surfaces.^{23,48}

2. Raman spectra of hydrates

The formation of THF and CP hydrates was confirmed by analysing the Raman spectra of these samples. The Raman spectra for pure THF, 19.1 wt% THF aqueous solution and THF hydrate are shown in Figure 4. The spectra obtained for these three THF systems are consistent with those reported by Prasad et al.,⁴⁹ Tulk et al.,⁵⁰ and Walrafen et al.⁵¹ The most prominent modes in pure THF are at 914 cm^{-1} , 1030 cm^{-1} and $2870\text{ to }2960\text{ cm}^{-1}$. The stronger modes at 914 cm^{-1} and $2870\text{--}2960\text{ cm}^{-1}$ are assigned to a ring breathing mode,⁴⁹ and an anti-symmetrical stretching mode of the CH_2 groups,⁵² respectively. The weaker mode at 1030 cm^{-1} is attributed to the C–O–C stretch. In the 19.1

wt% THF solution, the bands centred at 914 cm^{-1} for the pure substance degenerated and split into two bands centred at 892 cm^{-1} and 918 cm^{-1} , which can be attributed to the interactions between THF and water molecules.⁴⁹ However, for THF hydrate, the 914 cm^{-1} band shifted to 920 cm^{-1} without splitting, because the highly-ordered cage of water molecules prevents the interactions that occur in the liquid phase.⁵⁰ The OH stretching vibration spectra at 3252 cm^{-1} and 3445 cm^{-1} for the THF aqueous solution shifted for its hydrate to 3170 cm^{-1} and 3384 cm^{-1} , respectively. This shift is caused by the fact that the two lone electron pairs of the oxygen atom in the THF molecule engage in hydrogen bonding with water molecules in the aqueous solution, but do not engage in hydrogen bonding when in the hydrate structure.⁴⁹

Raman spectra of pure CP and CP hydrate are also shown in Figure 4. For liquid CP, the bands at 889 cm^{-1} , 2872 cm^{-1} , 2904 cm^{-1} , 2944 cm^{-1} and 2972 cm^{-1} represent the CH_2 stretching modes. All the bands of CP hydrate are right-shifted (e.g., 889 cm^{-1} to 896 cm^{-1}) from those of liquid CP. This high-frequency shift of the CH_2 stretching bands is due to the encaging of CP molecules in the large cavities ($5^{12}6^4$) of sII hydrate, which is in accordance with literature data.⁵³

The higher intensity of the peaks at 3200 cm^{-1} relative to the peak at 3400 cm^{-1} observed in THF and CP hydrate is consistent with the increased ordering of water molecules in the hydrate phase. The observation also agrees with the results reported by Hashimoto et al.⁵⁴ who reported the Raman spectra of HFC-32 hydrate for which the peak at 3200 cm^{-1} was larger than that at 3400 cm^{-1} . For the THF systems (Figure 4(b)), the intensity ratio of the OH stretch modes (I_{3200} / I_{3400}) in THF hydrate ($R_{\text{OH-H}} = 1.35$) is significantly higher than in bulk water ($R_{\text{OH-W}} = 0.87$) and in the 19.1 wt% THF aqueous solution ($R_{\text{OH-W}} = 0.84$), indicating increased proton correlation in the hydrate phase due to

the polyhedral clathrate structures.⁴⁷ For hydrate structures, the band at 3200 cm⁻¹ is more intense than the band at 3400 cm⁻¹ because of the greater tetrahedral ordering.⁵⁵⁻⁵⁷

The Raman spectra of the THF and CP hydrates formed in the four systems: i) pure water, ii) clean glass particles, iii) DMOAP-coated glass particles and iv) OTS-coated glass particles are shown in Figure 5. The hydrate-phase intensity ratio $R_{\text{OH-H}} = I_{3200} / I_{3400}$ was used as a measure of the ordered (intermolecular-mode) water content in each hydrate-containing system. However, the value of $R_{\text{OH-H}}$ obtained for the hydrates formed in the four systems did not show significant variation: $R_{\text{OH-H}} = 1.28\sim 1.35$ for THF hydrate and $R_{\text{OH-H}} = 1.33\sim 1.43$ for CP hydrate. The results indicate that the added particles had little impact on the OH stretching mode of water in hydrate phase. Schicks et al.⁵⁸ also reported that the shape of the OH stretching bands and intermolecular water vibration bands only depended on the structure of the hydrate, and were not influenced by experimental conditions such as temperature, pressure or composition.

3. Promotion effect of OTS-coated glass particles on hydrate nucleation

Figure 6 shows the relationship between the median induction time determined from the measured hydrate formation CPDFs shown in Figure 1 for various systems as a function of the Raman intensity ratio $R_{\text{OH}} = I_{3200} / I_{3400}$ prior to hydrate formation. Without agitation and in the absence of additives there were no experiments in which hydrate formation occurred within 48 hours. For such experiments a minimum induction time (of 48 hours) is plotted instead of a median. The OTS-coated glass particles promoted significantly THF and CP hydrate nucleation, reducing their median induction times to 2 and 7.8 hours, respectively. The introduction of clean and DMOAP-coated glass

particles showed some promotion effect on THF hydrate formation, which had median induction times of 9.6 and 6.5 hours, respectively, but had no effect on the formation of CP hydrates.

The presence of the surfaces increased the ratio of the OH stretching bands in liquid water from its value in the bulk ($R_{\text{OH-W}} = 0.87$) to about 1 near either the clean glass or DMOAP-coated surfaces. However, in the vicinity of the hydrophobic OTS-coated glass surface (water contact angle $> 100^\circ$), $R_{\text{OH-W}}$ increased to 1.23, which is significantly higher than that in bulk water, indicating that increasing the particle hydrophobicity makes the local water structure more ordered. Figure 6 shows a trend between the value of $R_{\text{OH-W}}$ measured prior to hydrate formation and the median induction time.

Moreover, the results in Figure 6 suggest that there may be an asymptotic relationship between the median induction time for hydrate formation and the difference in the ordering ratio for systems inside and outside the hydrate stability region, $\Delta R_{\text{OH}} \equiv R_{\text{OH-H}} - R_{\text{OH-W}}$. In these results a smaller ΔR_{OH} corresponded to a lower hydrate induction time. For the two types of hydrate (THF & CP), the average $R_{\text{OH-H}}$ was 1.34 ± 0.05 , and thus ΔR_{OH} increased sequentially: OTS-coated particles (0.11) < DMOAP-coated particles (0.34) $\approx$ clean particles (0.35) < pure water (0.47).

The CP hydrate median induction times reported here were larger than those observed for THF hydrates even when the level of water ordering was high, and when the subcooling temperature was larger (7.5 K vs 4 K). This reflects the low solubility of CP in the aqueous phase, and it is consistent with the MD simulation results of Walsh and co-workers^{4,59} who found for methane hydrates that guest molecule concentration in the aqueous phase was one of the most important factors affecting nucleation rate across a wide range of pressures, temperatures and interfacial geometries.

The experimental work of Li and Wang²⁵ has demonstrated that increasing the hydrophobicity of solid surface would increase the hydrate nucleation rate. This finding is consistent with the computational work of Bai et al²⁴ that hydrate nucleation can occur more easily on more hydrophobic surface. According to Skovborg et al⁶⁰, the driving force for hydrate nucleation can be defined as the chemical potential difference between water in the liquid and hydrate phase. Kashchiev and Firoozabadi⁶¹ derived estimates for hydrate nucleation rate, which is positively correlated with the driving force. Since the chemical potential of a water molecule near a hydrophobic surface is higher than in a bulk,⁶² the observed increase in the nucleation rate in the presence of hydrophobic surfaces can be at least partially accounted for by an increase in the driving force for clathrate hydrate nucleation.

SUMMARY AND CONCLUSIONS

The OH stretching mode of water molecules was analysed by Raman spectroscopy for water in the bulk and near surfaces with different hydrophobicity: (hydrophilic) clean glass particles, (partially hydrophobic) DMOAP-coated glass particles, and (hydrophobic) OTS-coated glass particles. The intensity ratio of the two Raman OH stretching bands centred near 3200 cm⁻¹ and 3400 cm⁻¹, respectively ($R_{OH} = I_{3200} / I_{3400}$), for liquid water near OTS-coated glass particles ($R_{OH-W} = 1.23$) was significantly higher than that in bulk water ($R_{OH-W} = 0.87$), indicating that the water molecules were more ordered near hydrophobic surfaces. Furthermore, an increase in R_{OH-W} (obtained prior to hydrate formation) was observed as the hydrophobicity of the glass particles increased, which in turn corresponded to a decrease in median induction times for THF and CP hydrates. Results for THF and CP hydrates together suggest there may be an asymptotic limit in the required induction time as R_{OH} approaches the value obtained for the clathrate hydrate phase ($R_{OH-H} = 1.34 \pm 0.05$). The value of

$R_{\text{OH-H}}$ observed for the hydrate phases formed in the various systems did not show any significant variation, suggesting that the glass particles had little impact on the OH stretching mode of water molecules within the hydrate phase.

These results derived from Raman spectroscopy are consistent with the templating component of hydrate nucleation mechanisms observed in MD simulations. They are also consistent with the increased water molecule structuring observed near hydrate-water interfaces by neutron scattering studies and the increased degree of water molecule ordering in the vicinity of hydrophobic surfaces by SFG studies. Furthermore, these new results help quantify the observations of hydrophobic surface-induced water molecule ordering with a promotion of hydrate nucleation in the vicinity of those surfaces. It may be possible in future work to compare quantitatively these experimental measures of water-ordering and hydrate nucleation promotion with the results of corresponding MD simulations, such as those of Bai et al.²³, involving surfaces with various degrees of hydrophobicity.

AUTHOR INFORMATION

Corresponding Author

*E-mail: liguang.wang@uq.edu.au.

Notes

The authors declare no competing financial interest.

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Figure 1. Induction time – formation probability distributions measured for THF hydrates on clean, DMOAP-, and OTS-coated particles, as well as for CP hydrates on OTS-coated particles. For THF hydrates in bulk water, and CP hydrates on clean and DMOAP-coated particles as well as in bulk water, no significant formation occurred for induction times less than 48 hours.

Figure 2. Raman spectra of dry clean, DMOAP-coated and OTS-coated particles used as baseline.

The value of the water contact angle, θ , measured for glass slides with the same coatings is also given.

(a)

(b)

Figure 3. (a) Example of a focus on water near the particle surfaces. The bright and round areas correspond to the glass particles, while the dark areas correspond to water. (b) Raman spectra for water measured in the bulk and near the particles prior to hydrate formation.

Figure 4. Raman spectra of the hydrate formers, THF (top) and CP (bottom), and their corresponding hydrates for the wavenumber ranges: (a) 800~1100 cm^{-1} and (b) 2800~3600 cm^{-1}

Figure 5. Raman spectra of (a) THF hydrate and (b) CP hydrate formed in four different systems: pure water, in the presence of clean, DMOAP-coated and OTS-coated particles, respectively.

Figure 6. Median (or, for values greater than 48 hours, minimum) induction times for THF and CP hydrates formation with various particle coatings as a function of ratio of Raman peak intensities at $\sim 3200 \text{ cm}^{-1}$ and $\sim 3400 \text{ cm}^{-1}$ prior to hydrate formation. These ratios were for liquid measured near the particle surface. The intensity ratios when hydrates had formed are also shown (average value across all particle types including bulk water).

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