Measurements of the Hydrate Phase via NMR and Raman Spectroscopy[1]

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ABSTRACT

A review of the literature on use of NMR and Raman spectroscopy to study the hydrate phase has been presented. NMR studies were carried out on the THF+water system to demonstrate the potential of NMR to study hydrates. Raman studies on the THF+water system are also reported to demonstrate the changes in the spectrum as hydrate forms. "Real time" Raman spectra of THF on THF hydrate formation are also reported. Raman studies were conducted on the CH_4+water system at elevated pressures and a weak peak corresponding to the C-H stretching band of CH_4 in the aqueous phase was observed at about 2910.5 cm^{-1}.

KEY WORDS: chemical shift; hydrate; methane; NMR; Raman; review; shoulder; spectroscopy; splitting of peaks; THF; water.

1. INTRODUCTION

The prediction of hydrate formation conditions is crucial for industrial development of energy reserves in unusual environments such as permafrost or deepwater Gulf of Mexico. Even though hydrate plugs in pipelines often occur, industries do not determine which crystal structure plugs each pipeline, because crystals are never collected and measured. Instead hydrate flow blockages are removed as quickly as possible. However, the hydrate structure must be known in order to accurately predict or inhibit formation thermodynamics and kinetics.

Even in laboratory experiments the hydrate phase is virtually never measured because macroscopic measurements of the solid have been hindered by water occlusion and by phase inhomogeneity. Instead gas phase rule variables (e.g. T, P, composition) are measured but the hydrate phase is predicted, using the model of van der Waals and Platteeuw (1959). While the model has served well in past years, recent work suggests limitations which can only be removed by measurements of the hydrate phase itself. In several cases the model was fit to the erroneous hydrate structure (Saito, Marshall, and Kobayashi, 1964). The fact that the model can be fit to (and subsequently predict) the incorrect crystal structure suggests the model is a means of data fitting, rather than an *a priori* prediction technique.

Since 1987, 28 structure H (sH) hydrate formers have been reported, many of which are incorrectly listed in industrially important references such as the API Databook, (Lippert et al. 1950) -where methyl-cyclopentane and methylcyclohexane are listed as sII formers-

and the Handbook of Natural Gas Engineering. (Katz et al., 1959) - where isopentane and methylcyclopentane are listed as non-hydrate formers. In addition, several other hydrate structures may exist. Dyadin et al., (1991) found four hydrate structures and Jeffrey (1984) proposed five additional hydrate structures; these structures have yet to be confirmed.

With the evolution of these new structures experimentalists must admit that they can only predict the hydrate structure which has formed. Since different structures form at different thermodynamic conditions, this causes questions about such vital parameters as the temperature and pressure of hydrate formation, and the composition of the hydrate phase.

This work reviews two modern tools which complement more established diffraction methods to measure the hydrate phase. Nuclear Magnetic Resonance (NMR) and Raman spectroscopy enable not only the identification of the hydrate structure, but also the determination of hydrate phase composition and hydration number, as well as kinetic information.

2. LITERATURE REVIEW

2.1. NMR of hydrates

The use of NMR to study gas hydrates was primarily initiated by Davidson and Ripmeester [1-7] and their co-workers a number of years ago. Ripmeester and co-workers, as well as a few other research groups, continue to lead the way in NMR studies of gas hydrates. Davidson and Ripmeester have also reviewed NMR in hydrate research with emphasis on ^{1}H and ^{19}F wideline NMR [8].

Davidson et al. [9] measured both ^{1}H linewidths and second moments of hydrates and deuterohydrates as a function of temperature for methane, ethane, propane, isobutane and neopentane/D_2S using continuous-wave methods. Measurements between 50 and 200 K on both sI and sII hydrates indicated that guest molecules undergo rapid reorientation at these temperatures. The additional broad feature in the spectra is assigned to the rigid host lattice water molecules. These type of spectra, where the narrow ^{1}H resonance line of the guest is superimposed on the broad ^{1}H resonance line of the host water over the temperature range of about 50 - 200 K, is a signature feature of clathrate hydrates.

Measurements on the analogous deuterohydrates showed that guests cease to undergo rotational motion at low temperatures except for CH_4 which exhibits a narrow line at temperatures as low as 2 K. Davidson and Ripmeester have reviewed a substantial body of work [8] regarding ^{1}H and ^{19}F measurements of second moments and relaxation times obtained as a function of temperature and the theoretical interpretation of these results for a wide variety of hydrates and deuterohydrates. Garg et al. [10] presented a general method to calculate wideline NMR lineshapes of rigid multiproton molecules and have compared the results of such calculations with clathrate hydrate spectra.

Collins et al. [11] obtained occupancy ratios for a number of sI hydrates using ^{2}H, ^{19}F, ^{31}P and ^{77}Se solid-state NMR. In some cases, magic-angle spinning (MAS) was employed. The experimentally determined occupancy ratios when used in combination with a theoretical expression for the chemical potential permits hydration numbers to be computed.

A few studies of hydrates and deuterohydrates using ^{2}H wideline NMR have appeared [8,11]. Spectra obtained as a function of temperature have been used to qualitatively describe molecular dynamics in hydrates [8]. Collins et al. have determined occupancy ratios for C_2D_4 and C_2D_4 hydrates [11]. To date, however, ^{2}H wideline NMR spectra have not been analyzed using sophisticated modeling techniques in order to calculate ^{2}H spectra based on various motional models [12, 13].

Natural gas hydrates have hydrocarbon molecules as guest components and are of both scientific and practical interest [14], and ^{13}C NMR is expected to yield particularly useful results. Ratcliffe and Ripmeester [15] have reported ^{13}C non-spinning, solid-state NMR spectra of CO_2 from 77 to 250 K. At temperatures near 200 K, analysis of the NMR data indicates that CO_2 rotates about the sI hydrate $5^{12}6^{2}$ cage symmetry axis and that the guest molecule's long axis is constrained to lie in a plane which makes an angle no greater than 31° with respect to the equatorial plane of the cage. At low temperatures the CO_2 guest motion is more restricted and is characterized by a distribution of motional modes.

Ripmeester and Ratcliffe [16] reported ^{13}C cross polarization, magic-angle spinning (CPMAS) spectra of methane sI hydrate and methane/propane sII hydrate at 193 K. Cage occupancy ratios were obtained from the CPMAS NMR spectra and were used to compute hydration numbers. The results clearly show that resolvable resonance lines of CH_4 in the sI $5^{12}6^{2}$, sII $5^{12}6^{4}$ and the sI and sII 5^{12} cages can be obtained using MAS. This result suggests that high-resolution, solid-state ^{13}C NMR should be useful in studies to determine composition of naturally occurring gas hydrates where mixed sI and sII structures may co-

exist. Fleyfel et al. [17] have reported a preliminary ^{13}C NMR study of the formation/dissociation of a methane/propane hydrate.

Ripmeester and co-workers were the first to report ^{129}Xe NMR spectra for Xe trapped in the 5^{12} and $5^{12}6^{2}$ cages of sI hydrate [18,19]. ^{129}Xe NMR is a valuable tool to probe the structure of hydrates because it is nearly the same size as CH_4 [14], has favorable NMR sensitivity and a large chemical shift range [20]. Ripmeester et al. [20] have reported isotropic ^{129}Xe chemical shifts as well as asymmetry parameters for Xe in the various cages of sI, sII and sH hydrates and clathrasil dodecasil-3C. A plot of the ^{129}Xe chemical shift versus the free radius of these well-defined cavities showed a linear dependence. These results indicate that ^{129}Xe NMR can be used to readily identify the hydrate structure present. Mehta [22] has also used ^{129}Xe NMR to measure occupancy ratios and hydration numbers.

A recently developed technique using optically enhanced or hyperpolarized ^{129}Xe permits recording of ^{129}Xe NMR spectra with sufficient sensitivity and time resolution so that the formation of xenon clathrate hydrates can be monitored [21]. Ripmeester and co-workers have recently reported a study using optically enhanced ^{129}Xe NMR to follow Xe hydrate formation on an ice surface with a time resolution of a few seconds [21]. The results indicate that the initial hydrate phase has many more occupied small cages than exist at equilibrium and that the equilibrium composition is reached within a few minutes. Mehta was also able to follow the conversion of Xe + Benzene sI hydrate to its equilibrium sII hydrate and the Xe + Benzene + Neohexane sI hydrate to its equilibrium sH hydrate on a much longer time scale [22].

2.2. Raman work on hydrates

The literature on Raman spectroscopy of hydrates is still in its infancy. However, the past few years have witnessed the extensive use of Raman spectroscopy in hydrate studies. One of the most recent attempts to highlight the clathrate-like nature of highly supercooled water was made by Walrafen [23]. He concluded from his studies on supercooled water and THF clathrate that highly supercooled water had a clathrate-like hydrogen bonded network of water molecules. Johari and Chew [24, 25] were the first to apply Raman spectroscopy to clathrate hydrates. They studied O-H and O-D spectra of water in THF hydrate.

Seitz [26] reported that Raman bands of CO_2 and CH_4 trapped in hydrates were shifted to lower frequencies compared to their gas phase frequencies. He observed splitting of the ν_1 C-H symmetric band for CH_4 and attributed it to methane occupying two different types of cavities (large and small). Seitz did not report any splitting of bands for CO_2.

In this laboratory, Sum [27] studied single and double hydrates of CH_4 in different hydrate structures. He also observed splitting of the ν_1 band for enclathrated CH_4, but Sum assigned the higher frequency band to the small cavity and the lower frequency band to the large cavity, in contrast to Seitz's assignments. Sum studied CH_4 and CH_4/CO_2 systems for sI; CH_4/THF-*d8* for sII; and CH_4/Methylcyclohexane-*d14* system for sH hydrate.

Sum was the first to use Raman spectra to determine hydrate compositions and cage occupancies. Table 1 summarizes the peak positions reported by Sum for CH_4 in different cavities of sI, sII, and sH. Figure 1 shows the Raman spectra obtained by Sum for CH_4 in each of the hydrate structures. Sum did not observe any band splitting for CO_2 and

concluded that CO_2 only occupied the large cavity. Koh [28] in a personal communication confirmed that she did not observe any splitting of the CO_2 band in her studies on hydrates.

In 1995, Masutani [29] reported spectra of CO_2 dissolved in water and CO_2 trapped in hydrates. Uchida [30] proposed a method to calculate the hydration number of CO_2 hydrates using Raman spectroscopy. The method used the spectrum for dissolved CO_2 as a reference spectrum.

Nakahara [31] in 1988 was the first to use Raman spectroscopy to study natural air clathrate samples that have been recovered as single crystals from deep ice cores in Greenland and Antarctica. He reported a N_2/O_2 ratio of 1.6-1.9 for these samples and suggested that fractionation of N_2 and O_2 might have occurred as hydrate formed from the trapped air bubble. In 1996, Pauer [32, 33] reported values of 3.5-3.7 for the N_2/O_2 ratio in air hydrates and concluded that there was no fractionation of N_2 and O_2 on hydrate formation. Fukazama [34] reported values that indicated fractionation.

Raman spectroscopy was also used by Hinsenberg [35, 36] to study phase transitions in N_2 hydrates. Hallbrucker [37, 38] used Raman spectroscopy to study O_2 and NO hydrates. He concluded that O_2 occupied only the large cavity of sII hydrate.

3. EXPERIMENTAL STUDIES IN THIS WORK

3.1. NMR studies

Figures 2a and 2b show solid-state ^{13}C NMR spectra of THF hydrate recorded at -6 °C and Figure 2c shows a liquid-state ^{13}C NMR spectrum of an aqueous solution THF (molar ratio H_2O:THF 17:1) recorded at 25 °C. The spectra were recorded at 100.6 MHz on an Otsuka Electronics CMX Infinity 400 NMR spectrometer. Chemical shift references (by sample substitution) were the methyl carbon resonance of HMB (assigned a chemical shift of 17.35 ppm) and the high-field methylene carbon resonance of pure THF (assigned a chemical shift of 25.37 ppm) for the solid state and liquid state, respectively. Comparison of the ^{13}C NMR spectra shows that the two methylene carbon resonance lines are both shifted by about 1 ppm to lower shielding values in the hydrate (26.3 and 68.4 ppm) relative to those of aqueous THF (24.8 and 67.6 ppm). The near equality of the ^{13}C chemical shifts in THF hydrate and the aqueous solution of THF suggests that the structure of the solvation shell of aqueous THF is, on the average, similar to that of the $5^{12}6^{4}$ cage occupied by THF in this sII hydrate. Also note that 1.0 KHz MAS effectively removes the small chemical shift anisotropy of the methylene carbons in the THF hydrate.

3.2. Raman studies

The Raman spectrometer used in this study was an Instruments SA Ramanor U1000 system. A custom-designed high pressure Pyrex cell was used to obtain the Raman spectra. Detailed discussions about the experimental setup and the high pressure Raman cell can be found in [27].

In this lab, Raman studies on THF clathrate were carried out by X Long [39]. Figure 3a shows the Raman spectrum of pure THF liquid under ambient conditions. Figure 3b shows the spectrum for THF:H_2O (1:17 mole ratio) solution at 3 °C, and ambient pressure. Figure 3c shows the spectrum for THF hydrate at 3 °C and ambient pressure. As can be seen in Figure 3b, a shoulder appears on the C-O-C 913 cm^{-1} stretching band for THF in solution. From Figure 3c, it is evident that this shoulder disappears when hydrates form. The shoulder was attributed to the existence of H-bonding between THF and water in solution. These H-bonds break when the clathrate forms from solution. Also, when hydrate forms, a band corresponding to the lattice mode appears at a lower frequency in the spectrum. Changes also occur in the O-H stretching water band. X. Long also obtained the first "real time" spectra showing disappearance of the shoulder as hydrate formed from a 1:17 THF:H_2O solution. This is illustrated in Figure 4.

Figure 5 shows the Raman spectrum of dissolved methane along with the O-H stretching band for water at 1500 psig and 15 °C. The dissolved CH_4 band is located at about 2910.5 cm^{-1}. This implies a shift of about 6.5-7.0 cm^{-1} compared to the gas phase. This peak lies in between the peaks for methane in the large and small cages of hydrates (Table 1). This observation may be useful in future Raman studies involving hydrate kinetics. This study is the first to report the position of the Raman band for CH_4 dissolved in water.

3.3. Future work with Raman & NMR spectroscopy

NMR and Raman spectroscopy can be used in a complementary manner to study both thermodynamic and kinetic aspects of hydrate research. These include hydrate phase composition studies, hydration number studies, cage occupancy calculations, rigorous testing of the van der Waals and Platteeuw hydrate equilibrium prediction model, etc. for different hydrate structures. “Real time” kinetics of methane hydrate nucleation and growth can be studied in situ by monitoring the Raman peak positions and intensities of methane in the gas, aqueous and hydrate phases. Kinetics of structural transitions in various hydrate systems can be studied (e.g. sI to sH [22]). It is also possible to measure kinetics of hydrate formation with inhibitors present in the aqueous phase. ^{13}C NMR studies can be done on real natural gas systems to address some of the issues mentioned above and hydrate samples recovered from nature can be analyzed using NMR.

4. CONCLUSIONS

The literature review provided in this paper for NMR and Raman work on hydrates indicates that these techniques are powerful tools to study the long-neglected hydrate phase. Valuable information regarding hydrate phase composition, guest cage occupancies, hydration numbers, kinetics of hydrate nucleation, kinetics of structural transitions, kinetics of growth, etc. can be obtained from these spectroscopic measurements. These tools can be invaluable in identifying new hydrate structures [40]. NMR and Raman techniques will clearly dominate hydrate phase studies at a molecular level in the coming years.

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List of Tables

Table 1

Peaks \ Hydrate	Hydrate structure		
	sI	**sII**	**sH**
Large cavity Peak position (cm^{-1})	$5^{12}\,6^{2}$ 2904.85 ± 0.33	$5^{12}\,6^{4}$ 2903.72 ± 0.28	$4^{3}\,5^{6}\,6^{3}$ 2905
Small cavity Peak position (cm^{-1})	5^{12} 2915.04 ± 0.58	5^{12} 2913.73 ± 0.76	5^{12} 2912.76 ± 0.3
# spectra analyzed	164	26	7

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Figure 1

Figure 2

Figure 3

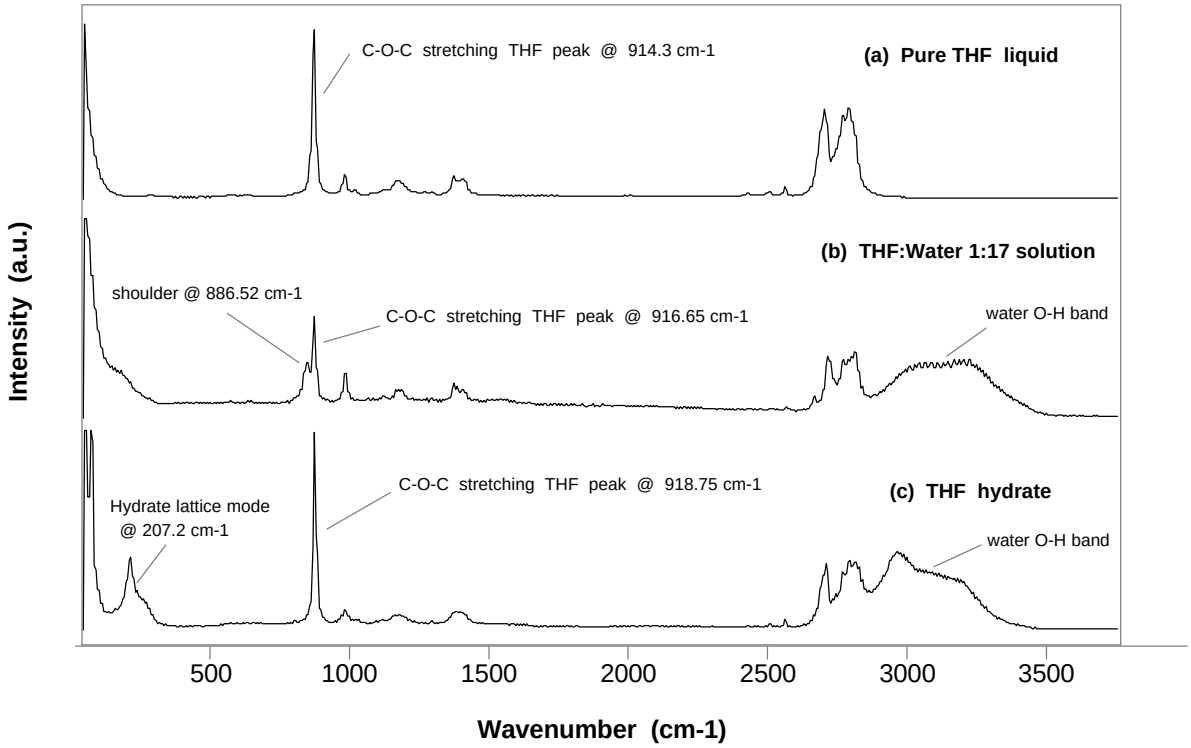
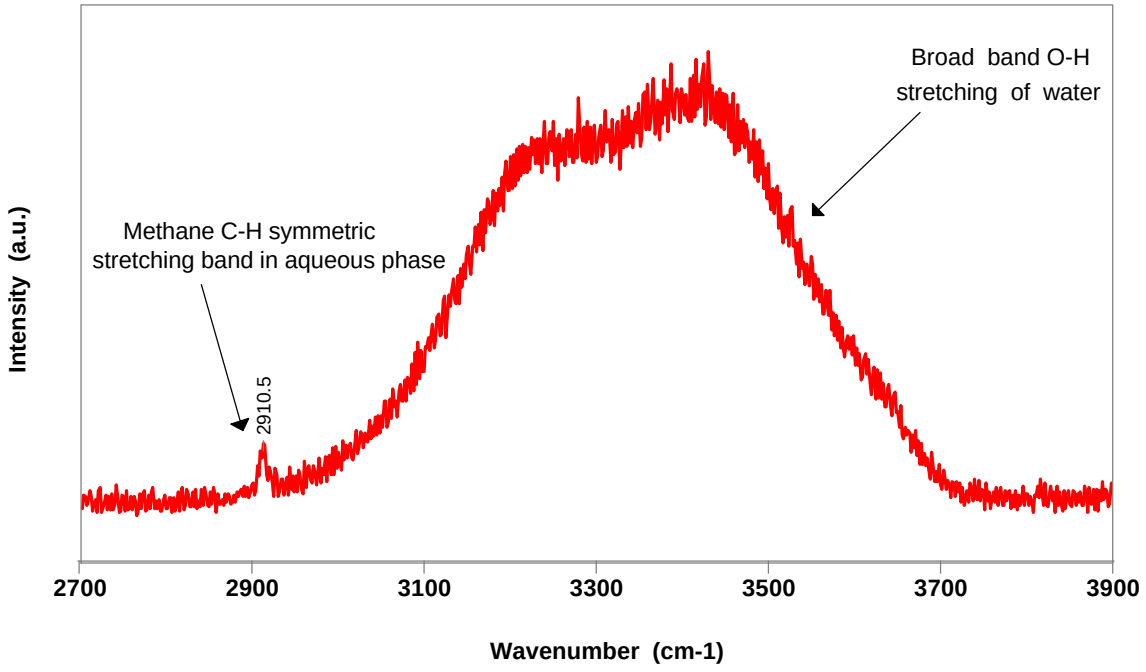

C-O-C stretching THF peak @ 914.3 cm-1
(a) Pure THF liquid
(b) THF:Water 1:17 solution
shoulder @ 886.52 cm-1
C-O-C stretching THF peak @ 916.65 cm-1
water O-H band
C-O-C stretching THF peak @ 918.75 cm-1
(c) THF hydrate
Hydrate lattice mode
@ 207.2 cm-1
water O-H band
Intensity (a.u.)
500
1000
1500
2000
2500
3000
3500
Wavenumber (cm-1)

Figure 4

Figure 5


Broad band O-H
stretching of water
Methane C-H symmetric
stretching band in aqueous phase
2910.5
Intensity (a.u.)
2700
2900
3100
3300
3500
3700
3900
Wavenumber (cm-1)