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Raman spectroscopic measurements of synthetic gas hydrates in the ocean

K.C. Hester [a], S.N. White [b], E.T. Peltzer [c], P.G. Brewer [c], E.D. Sloan [a,*]

[a] Center for Hydrate Research, Colorado School of Mines, Golden, CO 80401, USA
[b] Department of Applied Ocean Physics and Engineering, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA
[c] Monterey Bay Aquarium Research Institute, 7700 Sandholdt Road, Moss Landing, CA 95039, USA

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Abstract

A Raman spectrometer extensively modified for deep ocean use was used to measure synthetic hydrates formed in an ocean environment. This was the first time hydrates formed in the ocean have been measured in situ using Raman spectroscopy. Gas hydrates were formed in situ in the Monterey Bay by pressurizing a Pyrex cell with various gas mixtures. Raman spectra were obtained for sI methane hydrate and sII methane + ethane hydrate. Gas occlusion resulting from rapid gas growth of methane hydrate was measured immediately after formation. The Raman shift for methane free gas was coincident with that of methane in the small 5^{12} hydrate cage. The methane Raman peak widths were used to discriminate between methane in the free gas and hydrate phase. Methane + ethane sII hydrate was formed for 43 days on the seafloor. In this case, gas occlusion was not measured when the gas hydrates were allowed to form over an extended time period. Equivalent Raman spectra were obtained for the in situ and laboratory-formed sII methane + ethane hydrates, under similar p, T, and x conditions. With the Raman spectrometer operating in the ocean, seawater contributes to the Raman spectra obtained. Both the Raman bands for the sulfate ion and water were used to qualitatively determine the distribution of water phases measured (hydrate, seawater) in the Raman spectra.

Keywords: Monterey Bay; Gas hydrates; Raman spectroscopy; Structure I; Structure II

1. Introduction

Gas hydrates are non-stoichiometric, crystalline, inclusion compounds (Sloan, 1998). These compounds can enclathrate light gases such as methane, ethane, and carbon dioxide. Gas hydrates are formed when water and gas combine at high pressures and low temperatures. Hydrates form three common structures: sI, sII, and sH (Sloan, 1998). The sI unit cell, a primitive cubic lattice (*Pm3n*), consists of six large cages ($5^{12}\ 6^2$) and two small cages (5^{12}), formed from 46 H_2O molecules. Methane and ethane both form sI as pure components. The sII unit cell, a face-centered cubic lattice *(Fd3m)*, consists of eight large cages ($5^{12}\ 6^4$), 16 small cages (5^{12}), formed from 136 H_2O molecules (Sloan, 1998). Certain mixtures of methane + ethane can form sII, as well as pure gases of propane and i-butane. sH hydrates, which require a large guest such as methylcyclohexane along with a smaller guest like methane, are not considered here.

Gas hydrates were first discovered to exist in natural environments in 1965 (Makogon, 1965). Permafrost

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* Corresponding author. Tel.: +1 303 273 3723; fax: +1 303 273 3730.
E-mail address: esloan@mines.edu (E.D. Sloan).

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and oceanic environments have both the low temperatures and high pressures required for hydrate formation. Estimates (Kvenvolden, 1995) exceeding 10,000 gigatons of organic carbon, mainly in the form of methane, have been given for naturally occurring hydrate content worldwide (Collett, 2000). Because these estimates of in situ methane reserves are twice that of all other conventional reserves, much interest has been directed at natural gas hydrates from the energy sector (DOE, 1999). Methane is also an effective greenhouse gas and therefore dissociation of hydrates could have a significant impact on the environment (Kennett et al., 2002). Clearly, properties such as gas content of these natural clathrates are important for understanding past and future events relating to climate and the worldwide carbon cycle (Koh, 2002; Laherrere, 2000).

Vibrational spectroscopic measurements can provide insight into hydrate properties. Laboratory studies of clathrate hydrates using Raman spectroscopy have been developed over the last decade (Koh, 2002; Sum et al., 1997; Uchida et al., 1999). Vibrational modes of molecules shift in frequency as a function of a molecule's local environment (Long, 1977). These frequency shifts can be measured by Raman spectroscopy and allow discrimination between a molecule in the gas phase or in a discrete hydrate cage (Sum et al., 1997). Frequency shifts of a molecule's vibrational modes can be used to assign hydrate structure.

The Raman signal from water also shows variations between liquid and hydrate phases. Water O–H stretching modes give a very broad spectral feature (2800–3800 cm^{-1}) (Walrafen et al., 1997). The Raman spectra of the O–H stretching region can indicate that a solid water phase is present but cannot unambiguously be used to identify the hydrate structure present. Therefore, Raman signals for hydrate guests are typically used for assignment of hydrate phases present (Sum et al., 1997).

The fractional cage occupancy of a hydrate guest can be determined by integration of the area under the Raman bands. The ability to determine relative cage occupancies from Raman band areas has been verified against NMR spectroscopy with methane as the guest (Subramanian, 2000; Wilson et al., 2002). Raman band areas can be used for quantitative determination of hydrate occupancy when only one type of guest molecule is present. However, when more than one guest is present, Raman is only a qualitative tool. The reason is that, unlike IR spectroscopy, Raman intensities cannot be correlated simply with concentration (Subramanian, 2000). Raman intensities are also a function of a molecule's Raman scattering cross-section. For guest molecules in a binary or mixed hydrate, the scattering cross-sections do not change equivalently (Subramanian, 2000; Wilson et al., 2002).

With the recent development of the Deep Ocean Raman In Situ Spectrometer (DORISS) instrument (Brewer et al., 2004; Pasteris et al., 2004), it is now possible to analyze natural hydrates in situ using laser Raman spectroscopy. However, the problems of obtaining an accurate spectral characterization of a deep-sea hydrate specimen are still challenging. Hydrates themselves have a density less than sea water, and are kept in place only by weak attachment to the host sediments. Yet this sediment cover must be removed to permit laser probing of the exposed clathrate structure.

Interpretation of Raman spectra collected in situ in the deep sea requires comparison with laboratory measurements of synthetic hydrates and natural hydrates recovered by pressure coring. These comparisons are difficult for several reasons. The apparatus for in situ measurements was bathed in sea water. In order to acquire a Raman spectrum the laser beam was projected through a sea water path to excite the target molecules and to recover the scattered radiation. There was no difficulty in distinguishing hydrate guest molecules and the same molecules dissolved in seawater because the molecules were at such low abundance in natural sea water that they were far below the limit of Raman detection. In addition, some of the guest vibrational modes in hydrate were distinguishable from the modes for gas dissolved in water. However, the hydrate target itself is composed principally (~85 mol%) of crystallized water, and it would be useful to be able to estimate the contribution of the surrounding sea water to the recovered hydrated water signal.

Hydrate specimens recovered by conventional means (i.e. pressure coring) usually has some degree of dissociation to gas and liquid water during the recovery process. These specimens are then placed in liquid nitrogen for conservation and subsequent laboratory investigation (Tulk et al., 1999). Thus, water ice is usually present as a spectral signal, and yet this cannot be a real component of sea floor hydrates which are typically at temperatures at or greater 276 K. If in situ techniques are to present real advances, then one would like to be able to distinguish features in the spectrum that are characteristic of the hydrate cage alone. These features of the hydrate cages are well known from laboratory Raman studies (Sum et al., 1997) acquired with only air and a pressure vessel window in the optical path between the probe and the hydrate. Because small differences in the Raman frequency shifts of guests yield important structural features, refined calibration is necessary. For an in situ instrument, which is subject to large temperature and pressure changes, such calibration is a challenge.

For the above reasons, tests were undertaken to determine the accuracy of Raman spectra recovered in situ from hydrate specimens formed artificially in the deep sea. The object was to test the integrated system prior to investigation of natural specimens to determine the limits of signal recovery, and the contributions of the surrounding sea water.

2. Methods

2.1. Field laboratory Raman studies

In situ Raman measurements were obtained with MBARI's laser Raman spectrometer system DORISS deployed by remotely operated vehicle (ROV). This sea-going instrument is based on a laboratory model laser Raman spectrometer from Kaiser Optical Systems and consists of a 532 nm Nd:YAG laser, a holographically filtered probe head, a holographic duplex grating, and a 512 × 2048 front illuminated CCD camera from Andor Technology. The spectral range of DORISS is 100–4400 cm^{-1}. The duplex grating splits the spectrum into two strips on the face of the CCD chip providing a mapping of ~1 cm^{-1} per pixel. The instrument is packaged in three pressure housings connected by copper and fiber optic cables for use in the ocean to depths as great as 4000 m (Brewer et al., 2004). Power and communications to the instrument are provided through the ROV tether. The optical probe head with a stand-off sampling optic (10× objective, f/3.0 lens) is contained in a titanium housing with a dome glass window. A remote stage inside of the housing serves as a focusing mechanism by moving the probe head within the housing, providing a working distance of up to 152 mm in water. The spectrometer was calibrated in the laboratory prior to deployment. A diamond plate placed in the beam path of the laser inside the probe head serves as a calibration reference during deployment (Brewer et al., 2004; Zheng et al., 2001). The 1332 cm^{-1} diamond Raman line is superimposed on all collected spectra as a further calibration check.

To provide precision positioning of the DORISS probe head necessary for analyzing opaque targets, the Precision Underwater Positioner (PUP) is used (Kirkwood et al., 2003). PUP is a stand-alone positioner on which the DORISS probe head is mounted. It is off-loaded from the ROV onto the seafloor and can move the probe head in two dimensions with a precision of 0.1 mm. By mounting the probe head orthogonal to PUP's two axes of motion, the DORISS focus stage provides a third degree of freedom.

Two field deployments were carried out in August and December of 2003 in Monterey Bay. In August, the remotely operated vehicle (ROV) Ventana, operated from the R/V Point Lobos was used to deploy DORISS to mid-water depths of 500–900 m. Both DORISS and the hydrate sample cylinder were mounted onto a rigid

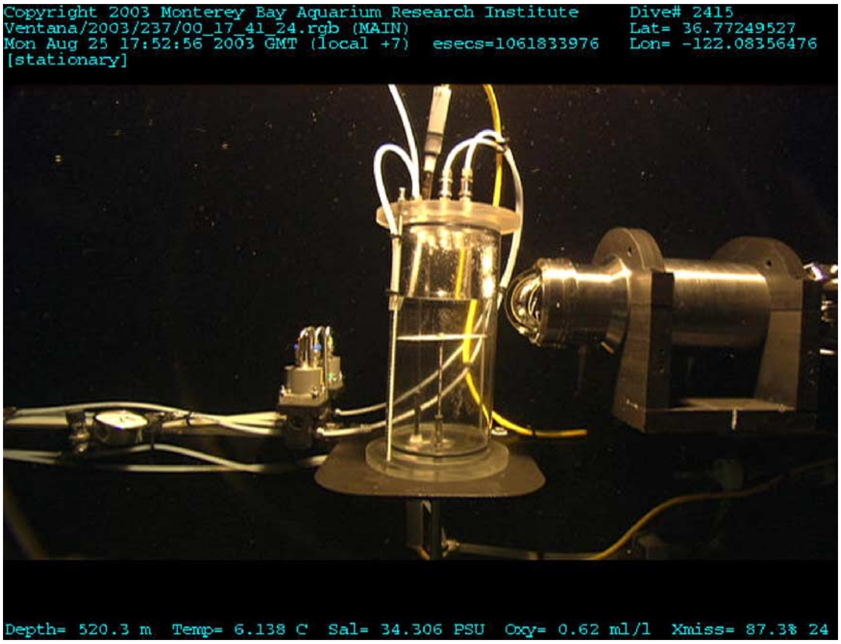

Fig. 1. DORISS and the hydrate sample cylinder mounted on a rigid frame on the front of the ROV.

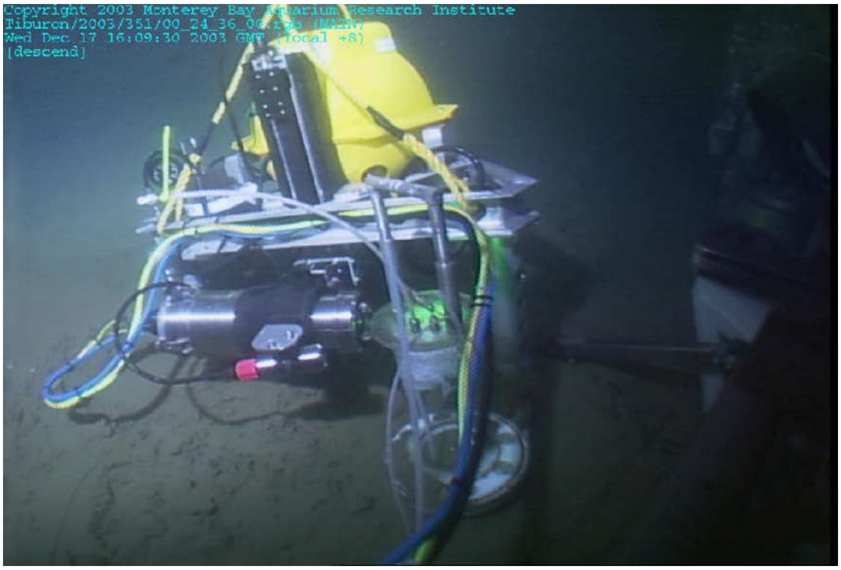

Fig. 2. Raman probe on PUP.

frame on the front of the ROV (Fig. 1). In December, DORISS and PUP were deployed on the seafloor at 1022 m depth by the ROV Tiburon (operated from the R/V Western Flyer, Fig. 2) to obtain data from a synthetic hydrate sample which was formed on the seafloor 43 days earlier.

Clathrate hydrates were formed in a 3.2 l cylindrical Pyrex tube (305 mm × 124 mm, Fig. 3) with sealed end caps containing gas/water lines. The cell was flushed with seawater during the descent. Gas was injected into the cell at depth from tanks containing previously prepared gas mixtures.

2.2. Onshore laboratory Raman studies

Onshore laboratory measurements were also performed using a Renishaw Inc. MK III Raman spectrometer equipped with a fiber-optic probe using a 20× objective. A 30 mW Ar^+ ion laser at a wavelength of 514.53 nm was used as the excitation source. Using a

Fig. 3. Clathrate hydrate cell on bench.

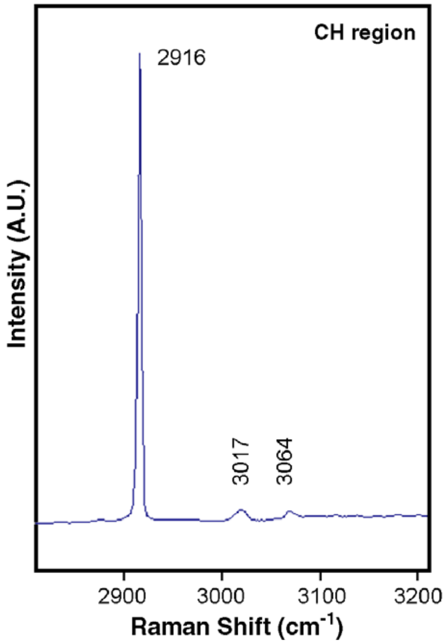

Fig. 4. Raman spectrum of methane gas (500 m, 278 K) with a collection of 375 s.

high-pressure, variable temperature 1 cm^3 sapphire windowed cell (Huo et al., 2003), conditions similar to field environments could be achieved.

Samples were formed from a mixture of water and free gas at high pressures. The water was injected into the temperature-controlled cell and degassed before the cell was pressurized with the hydrate-forming gas. The bulk of hydrate formation occurred at the vapor/liquid interface between those two phases. For hydrate measurements, the laser focus was adjusted slightly below the vapor/liquid interface in the water phase to avoid free gas contribution. The spectra were obtained and analyzed using Grams® software.

3. Field experiments and results

3.1. Ventana Dive 2415: August 25th, 2003, midwater at 500–900 m

Pure methane was used which forms a sI hydrate. Because the sampling volume for DORISS was very small, on the order of cubic microns, each phase (free gas, dissolved gas, and hydrate) could be measured independently. In order to measure the different phases in the cell (gas, hydrate, aqueous), the water level was adjusted using a pump. The pump also allowed fresh seawater to be brought into the cell following a hydrate formation experiment.

Pure methane was injected into the cell at 500 m. Using DORISS, the gas and liquid water phases were measured inside of the cell. The methane gas spectrum, shown in Fig. 4, was of excellent quality, even for a laboratory setting. This illustrates the unique ability of this modified Raman spectrometer to obtain pristine data in situ. The peak position of the ν_1 symmetric

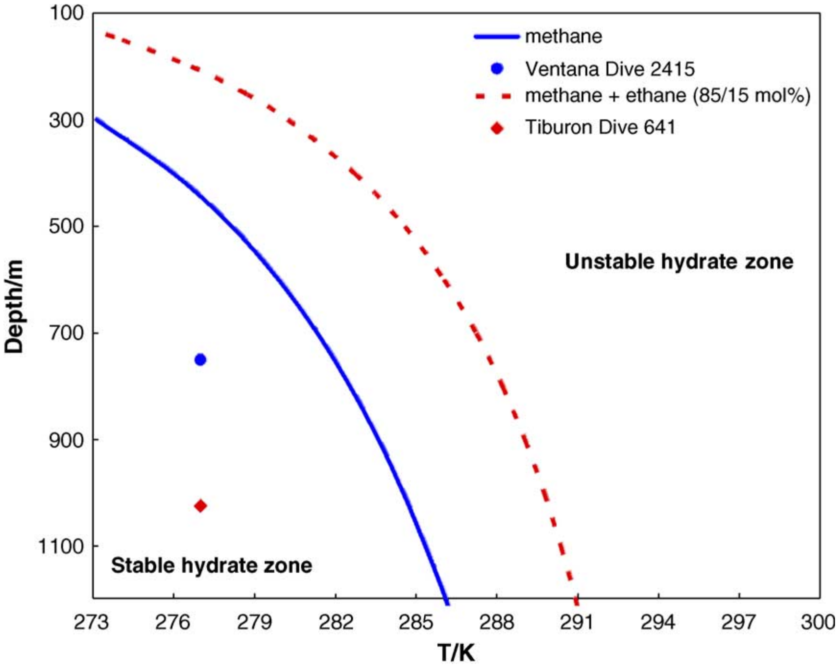

Fig. 5. Phase diagram prediction by CSMGem[12] for a methane+water and 85/15 mol% methane+ethane+water system.

Table 1
Summary of Raman shifts for materials measured in this study

Molecule	Vibrational mode	Raman shift (cm^{-1})	sI		sII		Aqueous
		Gaseous	$5^{12}6^2$	5^{12}	$5^{12}6^4$	5^{12}	
Methane	ν_1 (CH sym stretch)	2917	2915	2905	2914	2904	2910
Ethane	ν_3 (CC stretch)	994	1001		993		
	ν_1 (CH3 sym stretch)	2900	2891		2887		
	2 ν_{11} (CH3 d-stretch)	2955	2946		2942		
Sulfate	ν_1 (SO stretch)						981
Water	OH stretch		2800–3800 (liquid, sI, sII, ice phases)				

The OH stretching region for water is between 2800 and 3800 cm^{-1} for the liquid, sI, sII, and ice phases. The change with phase is the shape of this peak.

C–H stretch (around 2916 cm^{-1}) for methane agrees with expected values at the experimental pressure and temperature (Fabre and Couty, 1986).

Dissolved methane was not detected in the seawater due to the low solubility of methane in water and minimal time allowed for equilibrium. A small contribution from methane should be detectable, given a longer time.

The ROV proceeded to dive to 750 m during which hydrate formation at the gas/liquid interface was visually observed. The phase diagram (Fig. 5) for incipient hydrate formation (Ballard and Sloan, 2002) indicates that this depth was suitable for hydrate formation. Further hydrate formation appeared to be induced by agitating the interface with a wire mesh, causing heterogeneous nucleation and increased contact area between the gas and liquid phases. Hydrate particles began to stick and buildup on the wire mesh.

In order to measure the hydrate phase, the water level in the cell was adjusted so the laser focus was slightly below the interface, and so that hydrate accumulations on the mesh screen were positioned on the focal point. The hydrate was measured in the seawater because the ν_1 methane gas band overlaps with the ν_1 band for methane in the sI and sII 5^{12} cage. Table 1 shows Raman stretching bands for compounds used in this study. The laser was focused on a number of different regions on the hydrate surface. However, even in the seawater, the sI clathrate hydrate spectra had a strong signal from gaseous methane as shown in Fig. 6.

After the methane measurements were complete, the ROV depth was decreased to 300 m, to a pressure which allowed the hydrate to dissociate (see Fig. 5). After flushing the cell with fresh seawater, the ROV was returned to 500 m and a mixture of methane+ethane (80/20 mol%) was charged into the cell. Due to time restrictions, only the gas phase was measured.

3.2. Tiburon Dive 641: December 17th, 2003, seafloor at 1024 m

An 85 mol% methane–15 mol% ethane gas mixture was used to form a sII hydrate (Subramanian et al., 1999) in the clathrate cell and left on the seafloor on Ventana dive 2450 on November 05, 2003. During the descent on this dive, gas was injected into the cylinder every 200 m during descent and the cylinder was shaken to initiate hydrate formation. Clathrate hydrate was observed visually in the cell during the descent. Once on the seafloor, the gas line was mechanically cut to separate it from the ROV and the line was crimped to prevent gas release.

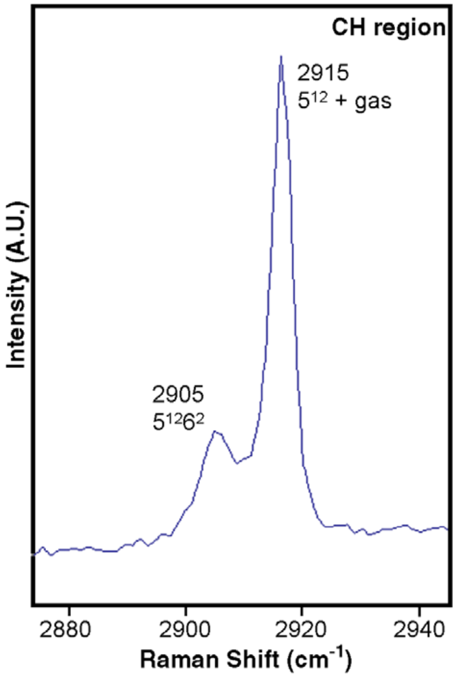

Fig. 6. Raman spectrum of methane hydrate+gas (750 m, 275 K) with a collection of 300 s.

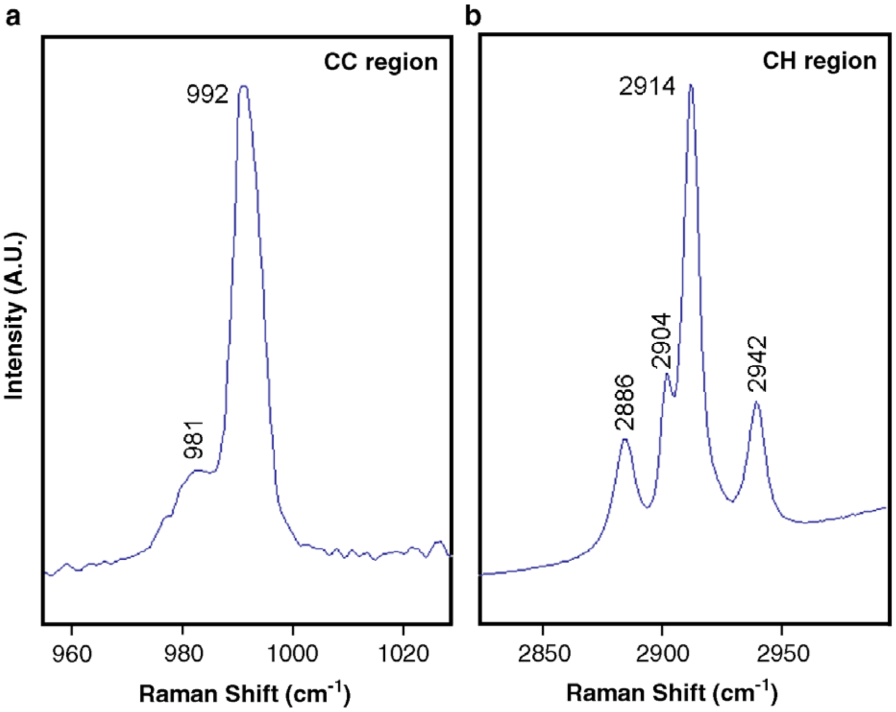

Fig. 7. Raman spectrum of methane+ethane hydrate (1024 m, 278 K) with a collection of 300. The peak at 981 cm^{-1} is due to the sulfate ion.

Upon the return during Tiburon Dive 641, clathrate hydrate had been allowed to form for over 40 days and appeared to fill the upper volume of the cell. The cell was moved onto the PUP system to allow measurements to be performed on the gas, hydrate, and aqueous phases.

Only small amounts of gas were measured, always accompanied by peaks due to sII hydrate. Methane dissolved in seawater was observed by the ν_1 band at 2910 cm^{-1}. No Raman bands from ethane in the seawater could be observed due to its low solubility in water.

sII hydrate spectra were measured by focusing on many areas of the hydrate phase. A representative spectrum is shown in Fig. 7. The assignment of sII was based on the ethane vibrational modes at 992 cm^{-1}, 2886 cm^{-1}, and 2942 cm^{-1}. These shifts are contrasted to the ethane bands in the gas phase (994, 2900, 2956 cm^{-1}) and in a sI hydrate (1001, 2891, 2946 cm^{-1}). These are summarized in Table 1. The methane peak positions and areas were also in agreement with the classification of sII (Subramanian and Sloan, 2002).

4. Discussion

The Raman spectra obtained from Ventana Dive 2145 was determined to be sI with free gas occluded, or trapped, in the hydrate phase. The assignment of methane in the sI large cage (5^{12} 6^2) was straightforward by its peak position at 2905 cm^{-1}. Methane in the small (5^{12}) cage was convoluted with methane in the gas phase. While the spectrum had the appearance of methane in a sII hydrate, the peak position as well as the peak width (full width at half maximum height or FWHM) can be used to discriminate between hydrate and gas phase contributions. The peak for methane in the 5^{12} cage has a position of 2915 cm^{-1} with a width around 7 cm^{-1}. At 750 m, the peak for gaseous methane is also expected around 2915 cm^{-1} at the experimental pressure but its width should be 4 cm^{-1}, as observed experimentally.

The measurement of strong gas contributions to the spectra can be explained by the ability of rapidly forming hydrate to occlude gas. As the hydrate forms, small pockets of gas can fill the hydrate matrix. The bulk hydrate acts as a diffusion barrier, slowing the transport of water to react with the occluded gas.

The Raman signal for water can be analyzed to further verify the formation of a hydrate phase. The O–H stretches of water form a broad spectral feature from around 2800 to 3800 cm^{-1}. Fig. 8a shows a comparison of the Raman spectra of seawater and sII methane+ethane hydrate. The spectra were normalized to the shared maximum around 3400 cm^{-1}. Overall, the

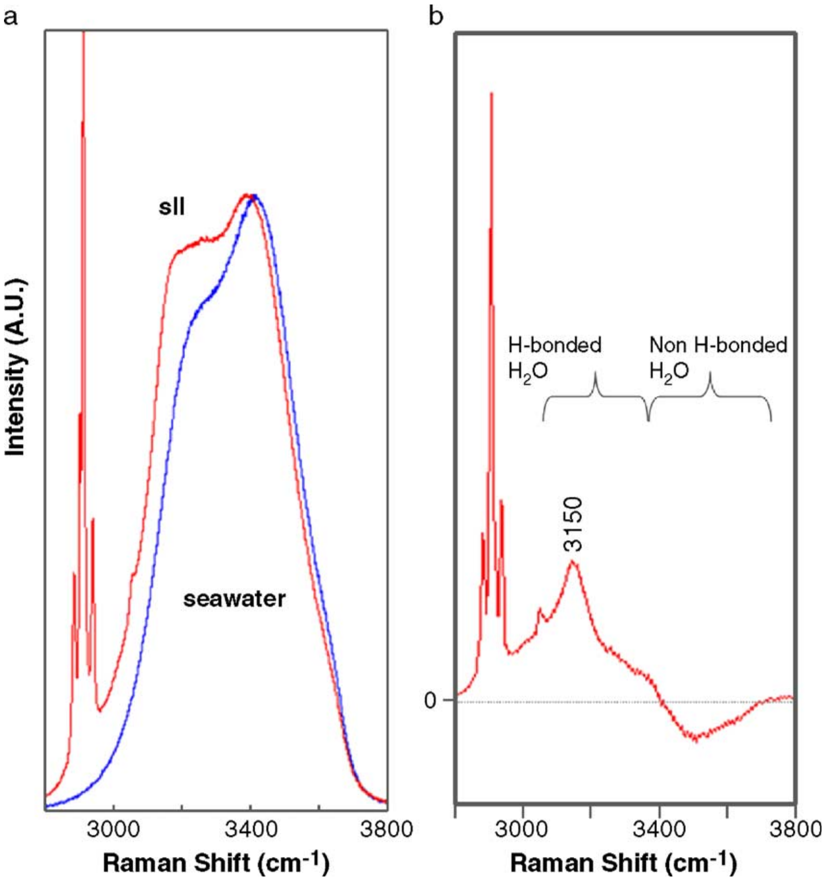

Fig. 8. Raman spectra of methane+ethane hydrate and seawater (1024 m, 278 K) normalized to maximum at 3400 cm^{-1}. O–H stretch of water shown. Panel b is the difference spectrum between the seawater and sII spectra.

O–H feature from 3150–3300 cm^{-1} of the hydrate greatly increases in intensity compared to the seawater spectrum. From 3400–3800 cm^{-1} the hydrate spectrum shows a slight decrease in intensity. A difference spectrum (Fig. 8b) emphasizes the variations in the spectra. As shown in Fig. 8b, a large maximum exists at around 3150 cm^{-1}. This maximum is attributed to increased proton correlation in the hydrate due to the polyhedral clathrate structures (Walrafen et al., 1997). Enhanced proton correlation occurs as the water molecules combine to form networks of five and six-membered rings. The ring formations increase the in-phase O–H stretching, and hence the proton correlation, of the individual waters, as a correlated movement of the ring. A negative difference is shown in Fig. 6b between 3400–3700 cm^{-1}. The negative difference indicates an increased number of H-bonded waters in the hydrate phase (Walrafen et al., 1997) compared to the seawater.

Because the Raman probe is immersed in seawater, some finite contribution from the seawater to the Raman spectra of the hydrate is inevitable. However, the seawater contribution poses no problem in the ability to successfully characterize the hydrate. The vibration of the hydrate guests alone have been shown to characterize the hydrate phase (Tulk et al., 2000). Because the guest vibrations can be used alone for structure determination, the water contribution is often largely ignored. Although hydrate structural properties can most often be determined without using the water Raman bands, the water modes must be considered if qualitative estimates of the seawater phase fraction are to be made.

Seawater contains the Raman active sulfate ion. Sulfate is excluded from the hydrate during formation. By monitoring the intensity of the sulfate band (~981 cm^{-1}) (Nakamoto, 1970), qualitative estimation of the phase fraction of hydrate versus the surrounding seawater being measured can be estimated. However, because guest bands can be used to derive hydrate properties such as crystal structure and fractional cage occupancy, the effect of the surrounding seawater on determining hydrate properties was minimal.

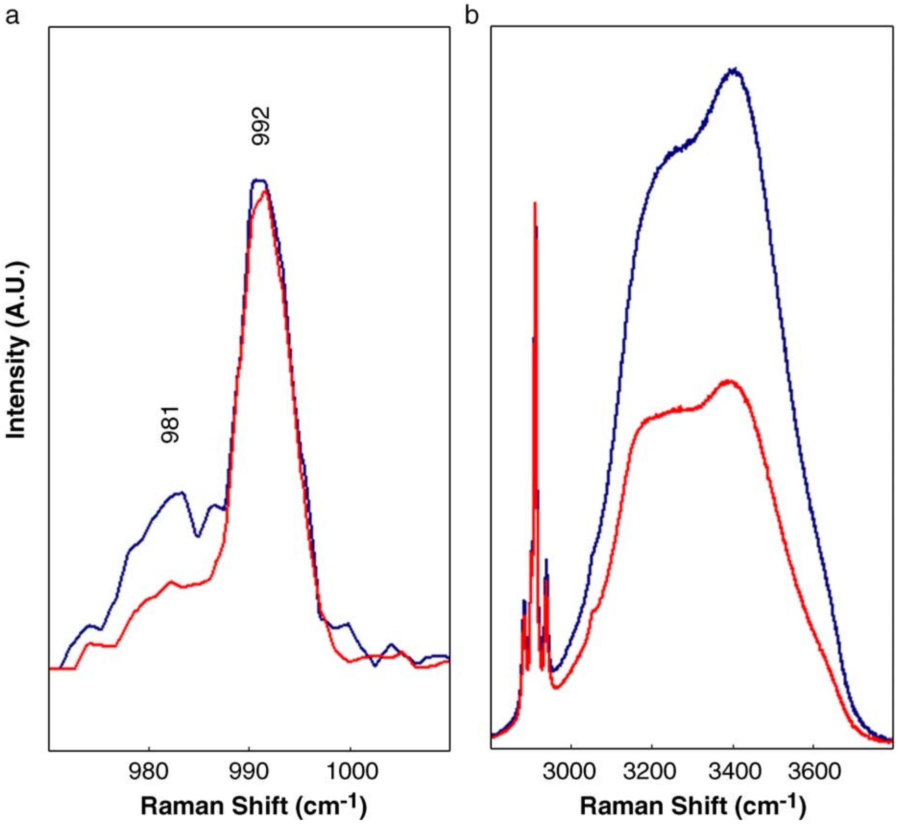

Fig. 9. Two Raman spectra of methane+ethane hydrate (1024 m, 278 K). Spectrum A contains greater phase fraction of seawater measured.

As the laser focus was adjusted on the hydrate, the amount of seawater measured in the spectra was minimized. Two separate spectra of sII methane+ethane hydrate were normalized in intensity with respect to the C_2H_6 ν_3 symmetric C–C stretch at 992 cm^{-1}, which corresponds to C_2H_6 in the 5^{12} 6^2 cage. This normalization corrected for variations in collection time and reflective losses. As seen in Fig. 9a, the sulfate peak in spectrum A is greater than that of spectrum B. This can be used to indicate that the seawater contribution is greater in A assuming the hydrate phase has a constant composition. If only the hydrate phase was measured, the sulfate band should be undetected (sulfate is excluded from the hydrate lattice). The higher seawater phase fraction measured in spectrum A is supported in Fig. 9b. Between 2800 and 3800 cm^{-1}, the O–H band from water is more intense in spectrum A because of the additional seawater present. Also, note the shape of the water O–H bands in spectrum A resembles more closely that of pure seawater (see Fig. 8) than spectrum B. Even with the additional contribution from the seawater, the presence of the sII hydrate phase could still be unambiguously detected in spectrum A as well as B from the guest molecule vibrations (Fig. 7).

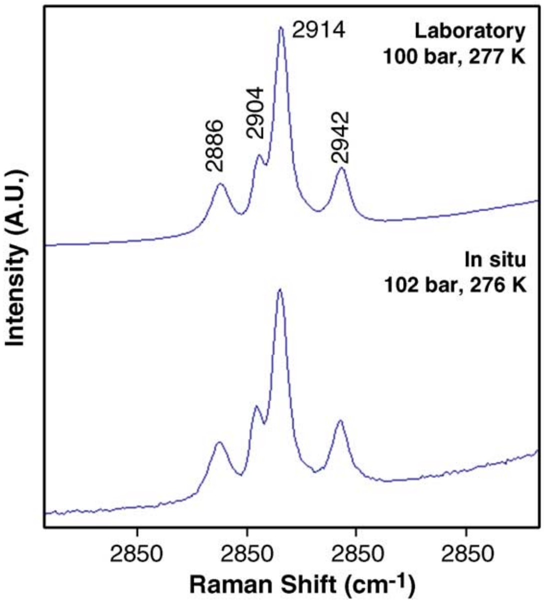

Fig. 10. Comparison of Raman spectra of methane+ethane hydrate measured in the field (1024 m, 278 K) and in the laboratory (100 bar, 278 K). The in-situ sample was formed from an 85/15 mol% methane+ethane. The laboratory sample was formed from an 85/15 mol% methane+ethane.

Fig. 10 shows the C–H stretching region (2800–3200 cm^{-1}) for the in situ hydrate (Tiburon Dive 641) and a hydrate measured in the laboratory under similar conditions (P, T, x) confirming sII hydrate is formed in both cases. Due to the qualitative nature of Raman spectroscopy, the band areas cannot be directly compared to give the gas composition in the hydrate. Although, when compared with one another, the field and laboratory hydrate spectra show reasonable agreement (Fig. 10).

5. Conclusions

Clathrate hydrates have been successfully measured for the first time in situ in an oceanic environment using Raman spectroscopy. Gas and liquid phases have also been investigated at ocean depths of 500 to 1000 m. Gas spectra obtained for methane and methane + ethane mixtures in the field agree with laboratory measurements at similar conditions. The field spectral quality is excellent, especially considering the measurements were made remotely deep in the ocean.

Rapidly formed methane hydrate occluded free gas inside of the clathrate. Because methane in the 5^{12} cage in both sI and sII and free gas peak positions are at similar frequencies, the free gas contribution can cause misinterpretation of the spectra. Extra caution must be taken to avoid errors when processing the spectra.

Methane and ethane was used to form sII hydrate in the hydrate cell at the seafloor over a 6-week period. Almost full conversion of the gas phase to hydrate was observed. The Raman measurements on the in situ sII clathrate hydrate were comparable to a sII hydrate sample measured in the laboratory.

Future work will extend the technique of Raman spectroscopy from laboratory and synthetic subsea hydrates to natural in situ hydrates on the seafloor. The work has confirmed that clathrate hydrates can be measured using Raman spectroscopy in a subsea environment.

Acknowledgements

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