Infrared Spectroscopy for Monitoring Gas Hydrates in Aqueous Solution

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ABSTRACT

The presented work describes first principles for monitoring gas hydrate formation and dissociation in solution by evaluating state-responsive IR absorption features of water with fiberoptic evanescent field spectroscopy. In addition, a first order linear functional relationship has been derived according to Lambert Beer's law, which enables quantification of percentage gas hydrate within the volume of water directly probed via the evanescent field. Moreover, spectroscopic studies evaluating seafloor sediments collected from a gas hydrate site in the Gulf of Mexico revealed minimal spectral interferences from sediment matrix components, thereby establishing evanescent field sensing strategies as a promising perspective for monitoring the dynamics of gas hydrates in oceanic environments.

Keywords: gas hydrates, infrared sensors, IR-ATR, evanescent field sensing, fiberoptics.

INTRODUCTION

With several exceptions, the application of infrared (IR) spectroscopy has historically been limited in gas hydrate research, which may be attributed to the rather strong IR absorption of liquid water encountered during conventional measurements.¹⁻⁸ transmission-absorption Nevertheless. transmission-absorption configurations have been utilized to investigate clathrate hydrate films grown from vapor deposition and epitaxial growth at highly reflective surfaces in vacuum chambers.¹⁻⁸ Formation of gas hydrates at these conditions has restricted the growth of simple hydrates for many of the natural gases, such as methane.¹⁻⁸

Recently, an infrared-attenuated total reflection (IR-ATR) study compared the spectral profiles of

CO₂(gas) and CO₂(aqueous) with that of CO₂(hydrate) for simple structure I (sI) CO₂ hydrates grown from aqueous solution.⁹ Although the phase-dependent transformations of water absorption features were not reported, a significant analytical advancement realized was bv confirming the capability of ATR techniques to spectroscopically study gas hydrates. In 2004, Zhang and Ewing reported a detailed evaluation of IR-ATR spectra for simple, sI SO₂ hydrates,¹⁰ which confirmed that IR-ATR techniques can be used to evaluate the phase transformation of water during hydrate growth.

In this study, the first principles for monitoring gas hydrate formation and dissociation in solution by evaluating state-responsive IR absorption features of water with fiberoptic evanescent field

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spectroscopy are introduced. In addition, a first order linear functional relationship has been derived according to Lambert Beer's law, which enables quantification of the percentage gas hydrate within the volume of water directly probed via the evanescent field. The quantification strategy is derived from shifts in the peak maximum corresponding to the 3^{rd} libration overtone $(3v_L)$ of water, which has also been referred to as the combination of the H-O-H bend and libration modes. The peak shift arises from the convolution of liquid and hydrate absorption spectra during the phase transition, which facilitates an intensity independent evaluation of the gas hydrate growth dynamics.

In this study, the developed analytical strategies have been utilized for continuous monitoring of hydrate formation and dissociation for simple clathrate hydrates of methane, ethane, and propane in deionized water for periods > 21 days. In addition, spectroscopic studies evaluating seafloor sediments collected from a gas hydrate site in the Gulf of Mexico revealed minimal spectral interferences from sediment matrix components (i.e., crude oils and minerals) on the described monitoring strategies. Hence, evanescent field sensing strategies are a promising perspective for the application of MIR chemical sensors in monitoring the dynamics of hydrate-bearing sediments in oceanic environments.

EXPERIMENTAL SECTION

Experimental chambers for laboratory growth of gas hydrates have evolved substantially since the initial discovery of clathrate hydrates.¹ In principle, hydrate growth chambers must be capable of attaining and sustaining conditions at or beyond the hydrate phase equilibrium, while providing the opportunity for manipulating and monitoring system parameters (i.e., temperature and pressure).¹

For this specific work, an already existing 304 stainless steel (SS) chamber with a sample volume of approx. 500 mL was modified to facilitate hydrate conditions and spectroscopic access.¹¹ Primary cooling of the sample volume was achieved by continuously flowing thermoregulated solution (50:50 water/ethylene glycol) through a 1/8" od. × 0.016" wall thickness 304 SS tube tightly wrapped into a 1" cooling coil at approx. 85 mL/min. The internal cooling coil provided approx. 9 continuous loops with 1.5" effective coil length.

A custom high pressure optical viewport (0.75" effective viewing diameter) was designed and fabricated, which provided access for visual inspection inside the sample chamber during hydrate measurements. A simple imaging system comprised of an Intel PC Camera (Model CS110, Intel Corporation, Santa Clara, CA) with universal serial bus (USB) interface enabled image capturing and viewing inside the hydrate growth chamber. The camera was interfaced with a desktop personal computer (PC) and controlled with Dorgem open source webcam capture software.¹²

The pressure and temperature logging system was developed using a VERSA1 programmable microcontroller development kit (Goal Semiconductor Inc., Montreal, Quebec; now Ramtron International, Colorado Springs, CO) with a Windows based user interface programmed using Microsoft Visual C++ (Dr. Frank Vogt, Applied Sensors Laboratory, ASL). The internal temperature of the hydrate system was monitored with a Model THX-400-NPT-72 1/4" MNPT pipeplug thermistor probe with a 2252 ohm resistance at 25 °C (Omega Engineering Inc., Stamford, CT). Pressure monitoring of the hydrate chamber sample volume was facilitated by a Sensor System Solutions, Inc. (3S, Inc., Irvine, CA) Model 5100 amplified media isolated silicon pressure transducer (Part No. 5100-B2-1000-A-P1) for operation in harsh environments up to 1000 psi (6.9 MPa). The pressure and temperature logging hardware and software contained a built-in pressure calibration for an Advanced Custom Sensors, Inc. (ACSI, now merged with 3S, Inc.) Model 8030-100 pressure transducer.

For spectroscopic access through a cross-section of the hydrate chamber, a fiber coupling system with custom-made PTFE ferrules and Swagelok components (Swagelok, Solon, OH) was implemented for a 300 mm × 700 µm diam. solidcore silver halide (AgX, $X = Cl_{0.3-0.4}Br_{0.7-0.6}$) fiber transparent from 3-15 µm. The optical setup for *in situ* spectroscopic monitoring of gas hydrate formation and dissociation was built around a Bruker IFS/66 Fourier transform-infrared (FT-IR) spectrometer (Bruker Optics Inc., Billerica, MA). Radiation modulated by the interferometer was guided outside of the spectrometer through a 45 mm od. optical port fitted with an IR transparent ZnSe window with anti-reflectance coating (MacroOptica, Moscow, Russia), and then focused onto the polished in-coupling facet of a $700 \,\mu\text{m}$ diam. solid-core AgX fiberoptic waveguide by a 2" dia. gold-coated off-axis parabolic mirror with a 3" focal length (Janos Technology, Keene, NH). IR radiation was guided via total internal reflection inside the AgX fiber through the hydrate chamber until reaching the polished out-coupling facet. The emanating divergent cone of radiation was collimated with another 2" diam. off-axis parabolic mirror, and then focused onto a Stirling-cooled mercurycadmium-telluride (MCT) detector element (Model K508, Infrared Associates, Stuart, FL) with a third 2" diam. off-axis parabaloid. The detected signal was processed with an impedance matched MCT-1000 pre-amplifier (Infrared Associates, Stuart, FL), and connected to an external input channel at the FT-IR spectrometer, as shown in Figure 1.

The primary function of the experimental setup developed in this study was to provide thermodynamically favorable conditions for gas hydrate formation, while enabling *in situ* spectroscopic monitoring of hydrate growth dynamics with IR fiberoptic evanescent field spectroscopy for the first time.



Figure 1 Optical image depicting the setup utilized for all IR fiberoptic spectroscopic studies monitoring gas hydrate growth and dissociation. The AgX fiber probes a cross-section of the pressure chamber via evanescent field absorption spectroscopy. The dashed (yellow) line indicates the radiation path.

Once the hydrate setup was assembled (Figure 1), the sample chamber was initially purged with copious amounts of supply gas. Following, the enclosed environment surrounding the setup was

purged with dry air to stabilize atmospheric humidity and CO_2 within the open radiation path. After stabilization, a reference spectrum was collected. Then, continuous spectroscopic measurements were initiated, and the pressure cell was filled with approx. 315 mL of aqueous solution, submersing the internal cooling coil and fiberoptic waveguide. Once filled, the chamber was pressurized with the supply gas followed by initiation of the cooling sub-system. Pressure and temperature data were logged throughout the entire measurement series. The hydrate setup was operated in a 'semi-closed' pressure environment; hence, hydrate growth was not at isobaric conditions. Hydrate dissociation was typically initiated by reducing the chamber pressure below the hydrate phase equilibrium with respect to the system temperature and supply gas.

GAS HYDRATE MONITORING

The focus of hydrate monitoring in this work centered on the evaluation of strong, phasedependent IR absorption signatures of water. Water has four primary IR absorption features, which can be used for monitoring gas hydrate growth and dissociation, as shown in Figure 2(a). A very intense, broad absorption feature is observed from 3750 - 2750 cm⁻¹ resulting from O-H stretch (v_{OH}) features. Peak positions observed for highly networked O-H stretches from gas hydrate structures (sI or sII) typically occur at approx. 3210 cm⁻¹, which corresponds to a red shift of approx. 120 cm⁻¹ with respect to reported values from the deconvoluted O-H stretches of liquid water at 25 °C.¹³

The second and lowest intensity absorption from approx. $2375 - 1875 \text{ cm}^{-1}$ corresponds to the 3^{rd} libration overtone $(3v_L)$. This peak maximum is strongly affected by temperature and liquid-to-solid phase transitions, which is consistent with the observed changes in the libration mode.¹³⁻¹⁵A blue shift for $3v_L$ of approx. 0.81 cm^{-1} per °C has been reported by Libnau et al.¹⁵ with peak maximum values for ice reported at 2190 cm⁻¹ @ - 6 °C,¹⁴ 2222 cm⁻¹ @ 0 °C,¹⁶ 2235 cm⁻¹ @ - 175 °C,¹⁷ and similar values reported throughout the literature.¹⁸⁻²⁰

The strongly absorbing H-O-H bend mode (v_2) occurs at 1750 – 1500 cm⁻¹. Upon phase transition and formation of rigid lattice networks of ice or gas hydrate, the overall absorption intensity of this feature is significantly quenched. The decreased v_3

intensity results from a loss in the induced transition dipole moment from the bending motion with increased coordination in H-bonded lattices.¹³ The libration (v_L) or frustrated rotation feature exhibits an intense absorption feature < 1000 cm⁻¹. In liquid water, this absorption feature has been shown to occur around 675 cm⁻¹ (below the cut-off of the used MCT detector),¹³ and the peak position is strongly affected by temperature and water phase, such that decreasing temperatures and/or formation of solid water structures result in a significant blue shift (peak maximum observed at 850 cm⁻¹ for ice at -20 °C as reported by Brubach et al.¹³, and 750 cm⁻¹ for ice at -4 °C as reported by Millo et al.¹⁴

Figure 2(a) displays changes in IR absorption signatures of water, as it transitions from liquid to solid (methane gas hydrate) state. In addition, Figure 2(b) presents to our best knowledge the first *in situ* recorded IR absorption spectra generated for simple clathrate hydrates of methane, ethane, and propane. These absorption spectra present similar spectral changes upon the phase change from liquid water (Figure 2(a)) to solid gas hydrate structures (regardless of sI or sII).



Figure 2 Fiber-optic IR-ATR spectra for (a.) liquid water and methane hydrate with labeled

absorption features for water and indication to spectral changes during the formation of gas hydrate, and (b.) methane (sI), ethane (sI), and propane (sII) hydrates illustrating the similarity in spectral shifts observed for each clathrate hydrate structure.

The collective evaluation of all major water absorption features provides the highest amount of information regarding sample contents interacting with the evanescent field throughout the phase transition of water from liquid-to-hydrate and hydrate-to-liquid. Figure 3 provides a spectral analysis respective to each of the water absorption features utilizing peak area analyses for v_{OH} , v_2 , and v_L , and peak position for $3v_L$ for a propane hydrate experiment in deionized water over a period of approx. 29 days.

The impact of temperature on liquid water absorption features can be observed in the analyses of the O-H stretch absorption intensity, libration absorption intensity, and peak maximum of the 3rd libration overtone during initial cooling stages starting on day 1, and concluding on day 3. In addition, temperature effects on the absorption behavior of liquid water are observed on day 27 (~6 °C) and day 28 (~24 °C) following hydrate dissociation. No discernable temperature effects were indicated in the H-O-H bend absorption intensity. Occasional spikes in the H-O-H bend intensity resulted from fluctuations in environmental humidity relative to conditions during collection of the initial reference spectrum.



Figure 3 Analyses of fiberoptic evanescent field spectra with respect to each of the four absorption features of water for a propane hydrate trial grown from DI water. (The data gap is the result of instrument down-time for servicing.)

Intensity changes in the O-H stretch and libration modes provide information regarding the formation of gas hydrate, whereby increased peak areas indicate the propagation of hydrate growth. The absorption intensity of the H-O-H bend mode provides similar information; however, amplitude changes are inversely related to hydrate growth; decreased peak areas are the result of increasing hydrate content. Lastly, the peak maximum of $3v_{\rm L}$ provides an intensity independent measure of hydrate content with a functional relationship to the %Hydrate directly interacting with the evanescent field. Hence, the intensity independent evaluation of chamber contents from $3v_L$ coupled with inversely related amplitude responses from the respective v_{OH} , v_L , and v_2 features provide a powerful combination for monitoring the overall propagation of hydrate growth and identifying spectral changes resulting from variable water content within the evanescent field (i.e., liquid water levels dropping below the fiber resulting in a decrease of water volume at the fiber surface).

QUANTIFICATION

Fiberoptic IR-ATR spectra collected throughout the liquid-to-solid phase transitioning of water represent the convoluted spectral contributions from all sub-structures of water interacting with the evanescent field. The IR spectrum of water (W) obtained during the formation of gas hydrate can be treated as the sum of absorption contributions from a binary phase mixture of liquid water (Liquid) and gas hydrate (Hydrate). Thus, W can be described following the Lambert Beer law as the equation:

$$W = A_{\text{Liquid}} + A_{\text{Hydrate}} \tag{1}$$

where $A = a \times C \times l$; A is the absorbance, a is absorptivity, C is the concentration (defined as mass-to-volume (m/v) in this work), and l is the optical pathlength. The effective optical pathlength l, for fiberoptic ATR waveguides is the net volume interrogated by the evanescent field given in an approximation by N, the number of reflections with an effective penetration depth d_e , over the entire fiber measurement surface and length. Hence, l can be defined as an effective measurement volume, where $Nd_e = V_l$. Both liquid water and hydrate can exist independently or coexist within V_l ; therefore, the following must hold true for the volume occupied by liquid (V_{Liquid}) and/or hydrate $(V_{Hydrate})$ within V_l ,

$$V_{\text{Liquid}} + V_{\text{Hydrate}} = V_{\text{Water}} \le V_l$$
 (2)

The first-order linear quantification strategy derived to approximate %Hydrate in V_l is based on the intensity independent evaluation of the peak maximum for the 3rd libration overtone. Thus, this technique provides a non-volumetric assessment of %Hydrate within V_l defined by the proportion of Liquid:Hydrate contributing to W (i.e., the sum of liquid and hydrate volumes can be less than V_l), and assumes negligible scattering losses arising from the formation of hydrate within d_e .

The first-order boundary conditions for the $3v_L$ peak shift are defined by the pure phases, where 100% Hydrate yields the upper peak maximum limit $\omega_{Hydrate}$, and the 100% Liquid peak maximum ω_{Liquid} , defines the lower limit. The mixture of both phases is defined as $\omega_{(Hydrate + Liquid)}$ such that:

$$\omega_{\text{Hydrate}} > \omega_{(\text{Hydrate+Liquid})} > \omega_{\text{Liquid}}$$
 (3)

Hence, $\omega_{(Hydrate + Liquid)}$ varies linearly in response to changes in %Hydrate within V_l, and shifts in peak position changes are independent of changes to V_{Water}. As the peak position of the $3v_L$ feature is highly sensitive to temperature (*T*), a general functional relationship can be derived:

$$\omega_{(\text{Hydrate+Liquid})} = f(\% \text{Hydrate}_{V_{I}})_{T}$$
(4)

Assuming that the Lambert Beer law is valid from 0 to 100% Hydrate in the described measurements, the shift in $\omega_{(Hydrate + Liquid)}$ follows a first-order linear relationship with respect to changes in %Hydrate within V_l.

The reported peak maximum of $3v_L$ for ice is minimally influenced over a fairly wide range of temperatures. In literature and the present study, the peak maximum of $3v_L$ for liquid water is strongly affected by temperature, which has been related to the temperature dependent structuring of H-bonded networks. Thus, equation 4 must be solved with respect to the peak position of $3v_L$ corresponding to the bulk system temperature. Using the established relationship between ω_{Liquid} and temperature in this study - for $T = 5 \ ^{\circ}C$ (approx. that observed at Mississippi Canyon MC118) - an initial ω_{Liquid} (100% Liquid) value of 2129.3 cm⁻¹ is obtained, and assumed to remain constant. If a ω_{Hydrate} (100% Hydrate) value of 2215 cm⁻¹ is implemented (average obtained for IR measurements of methane, ethane, and propane hydrate trials), the following mathematical relationship is derived:

$$\frac{\omega_{(\text{Hydrate+Liquid})} - 2129.3}{0.857} = \% \text{Hydrate}_{V_l} \quad (5)$$

Application of this quantification technique upon data from Figure 3 is presented in Figure 4. Figure 4 illustrates the localized growth dynamics of propane hydrate as %Hydrate from evaluation of $3v_L$ with an average pressure corresponding to approx. 475 ± 35 m of ocean depth, and an average temperature of 2 ± 1.5 °C from 1.5 days into the trial until approx. day 29. For this evaluation, ω_{Liquid} was defined as 2133 cm⁻¹ (average peak position for 50 measurements prior to nucleation), and $\omega_{Hvdrate}$ was defined as 2215 cm⁻¹. The derived fit equation (analogous to Equation 5) was utilized for data evaluation at all system temperatures (T_{system}); therefore, %Hydrate values correspond to 100% Liquid when $T_{\text{system}} > T$ for the defined ω_{Liquid} . From Figure 4, the highest %Hydrate valued observed in V_l during this trial was approx. 78%, which occurred around day 25.



Figure 4 Plot of calculated %Hydrate within V_l during a propane hydrate trial following spectroscopic analysis of $3v_L$. This hydrate trial was carried out at pressures comparable to oceanic environments in the Gulf of Mexico (GoM) with documented hydrate occurrences.²¹ IR-ATR spectra were an average of 250 sample scans with 0.5 cm⁻¹ resolution collected at 6 min intervals.

For quantitative applications in oceanic environments, additional factors affecting the $3v_{\rm L}$ peak maximum including temperature should be considered for accurate %Hydrate assessments as salinity and alkalinity (pH) can affect ω_{Liquid} , and both can vary with time and location. However, temperature is anticipated to impart the greatest effect on ω_{Liquid} with $\Delta \omega_{\text{Liquid}}$ of ~1 cm⁻¹ per °C. As salt ions are not incorporated into hydrate lattices, $\omega_{Hydrate}$ should remain relatively constant over a wide range of environmental conditions for small volumes interrogated by evanescent field sensing strategies. As a result, initial applications with only temperature considerations to the peak maximum $3v_L$ on ω_{Liquid} facilitate a reasonable first approximation for evaluating temporal changes in %Hydrate content within V_l.

Fundamentally, quantification is confined to the localized sample volume interrogated by the evanescent field, which does not guarantee representation of bulk hydrate growth behavior. Thus, this method is particularly well-suited for monitoring small-scale hydrate dynamics. Further spectroscopic studies are necessary to realize the full potential of performing accurate quantitative IR analysis of gas hydrates at harsh oceanic conditions. However, the potential value of monitoring short- and long-term changes in %Hydrate within oceanic gas hydrate ecosystems substantiates continued investigations to test and derivations improve mathematical for the described quantification strategies, and the development of deployable miniaturized MIR sensing platforms capable of operating in harsh oceanic environments.

IN SITU MONITORING

A primary objective of this study was to assess the **IR-ATR** initial feasibility for extending spectroscopic hydrate monitoring strategies into oceanic environments. A potential hydrate monitoring application for MIR chemical sensors could be embedding a sensing platform within hydrate-bearing sediments to for the first time monitor temporal hydrate dynamics in situ. Such an application would provide valuable data for assessing seafloor stability within marginal hydrate stability regions (shallower depths or at the base of hydrate stability zones due to geothermal gradients), whereby minor temperature or pressure changes could stimulate wide-spread, rapid dissociation events.²¹

To further assess the real-world feasibility of such an application, it was essential to screen sediment matrices for potential spectral interferences that could prevent detection and/or monitoring of gas hydrates with future development of deep-sea MIR chemical sensors. To facilitate this evaluation, a number of shallow (< 30 cm) box core sediment samples were collected around the Mississippi Canyon MC118 gas hydrate site for spectral analysis of sediment signatures from a variety of settings surrounding the hydrate system. Sediment samples were evaluated in their "native" hydrated (wet) condition without manipulation beyond collection, transport, and storage procedures. analysis facilitates a close Hence, this approximation as to what sediment spectral signatures would be occurring in the natural environment.

Figure 5 provides representative IR-ATR spectra for hydrated sediments with generic labeling of major mineral component absorption features and enables the direct assessment of potential interferences and limitations of data analysis procedures described for monitoring water absorption features during gas hydrate formation and dissociation with respect to sediment matrix components.



Figure 5 IR-ATR spectrum of hydrated sediments from the BC12 location at MC118 (All spectra were the average of 100 sample scans collected at 1 cm^{-1} resolution).

Despite complex sediment matrix compositions (e.g., quartz, clay, carbonate, and crude oils), IR-ATR spectroscopic evaluation of native sediment matrices revealed very limited overlap with three of the primary water absorption features; the O-H stretch, the H-O-H bend, and the 3^{rd} libration overtone. Although the $3v_L$ absorption region exhibited the least spectral contributions from

sediment components, data evaluation strategies implemented for evaluating gas hydrates in this study enable the use of all three water features with minimal interferences anticipated from nonwater components. Thus, sediment evaluations further support the feasibility of extending IR hydrate monitoring strategies into oceanic environments. Despite limited use of the libration band, the three available absorption features, each of which respond differently to hydrate growth, should facilitate the robust direct evaluation of hydrate dynamics in oceanic sediments.

CONCLUSION

This presented paper the first studies demonstrating the development, application, and assessment of fiberoptic IR-ATR spectroscopic sensing strategies for in situ monitoring gas hydrate formation and dissociation in aqueous environments. The first principles for monitoring gas hydrate formation and dissociation in solution by evaluating state-responsive IR absorption features of water with fiberoptic evanescent field spectroscopy were described. Examination of IR spectral profiles from sediment matrices collected around the MC118 reveled that sediment components have minimal impact upon data evaluation strategies tailored for examination of the O-H stretch, H-O-H bend, and 3rd libration overtone features. Furthermore, propane hydrate extending > 21 days demonstrated trials considerable long-term stability of this measurement strategy, which substantiates the for long-term deployments potential of submersible MIR chemical sensing platforms for environmental hydrate monitoring applications, as currently developed by the authors.

In addition, a first order linear functional relationship has been derived, which enables quantification of the percentage gas hydrate within the volume of water directly probed via the evanescent field. The quantification strategy is derived according to shifts in the peak maximum corresponding to the 3rd libration overtone of water. Finally, the quantification capability over a broad range of hydrate compositions substantiates practical use for initial evaluation and quantitative approximation to the variability of hydrate dynamics in harsh oceanic environments.

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