Characterization of Gas Hydrates using Raman Spectroscopy

Michael J. Lance

Metals & Ceramics Division

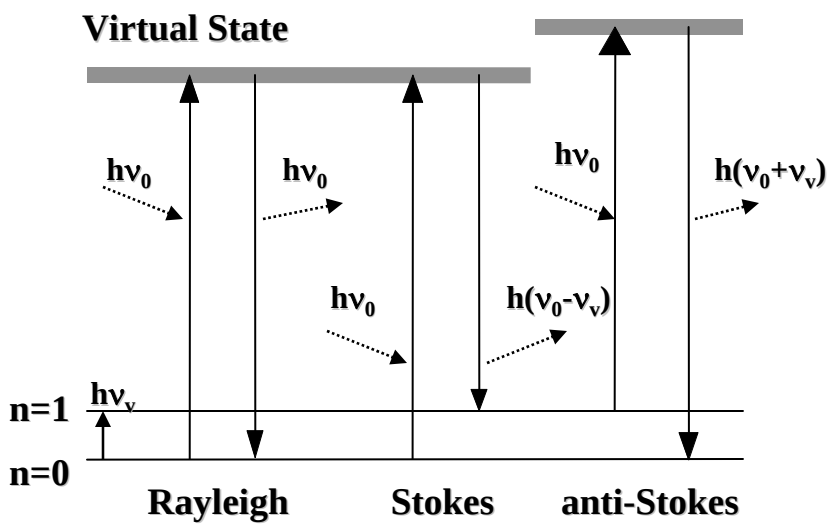
ORNL

Outline

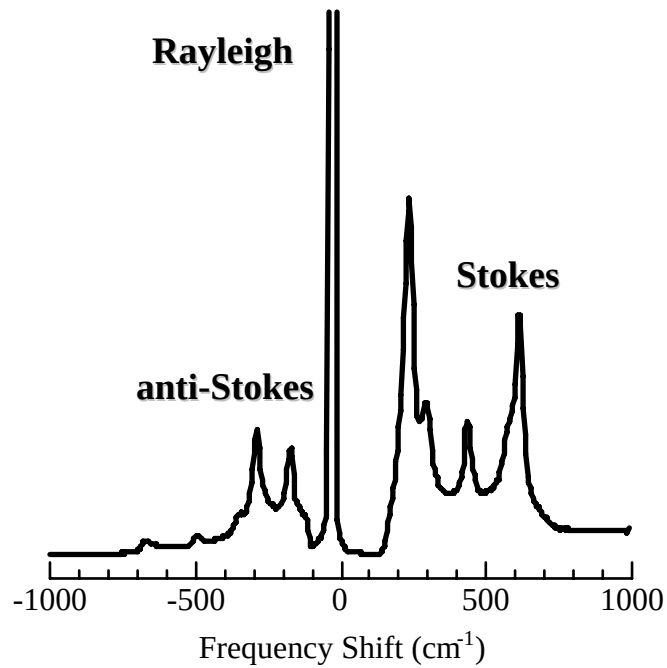
- Raman Spectroscopy
- Experimental Facilities
- Published Work
  - S. Subramaniam, M.J. Lance, C.J. Rawn, B.C. Chakoumakos, A.J. Rondinone, "Raman spectroscopic studies on structure I and structure II trimethylene oxide hydrate," *Can. J. Phys.* **83** [9] 941-949 (2005).
  - M.O. Gborigi, D. Riestenberg, M.J. Lance, S.D. McCallum, Y. Atallah, C. Tsouris, "Raman Spectroscopy of a Hydrated CO_2/Water Composite," accepted for publication *J. Petroleum Sci. Eng.* (2006).
  - Bryan C. Chakoumakos, Yoshinobu Ishii, Claudia J. Rawn, Hsin Wang, Jane Y. Howe, Michael J. Lance, Adam J. Rondinone, Camille Y. Jones, and Roger Sassen, "Physical Properties of Gas Hydrate from Green Canyon, Gulf of Mexico," submitted to *American Mineralogist* (2006).

The Raman Effect

Vibrational Energy Levels Showing the Interaction of Light With Matter

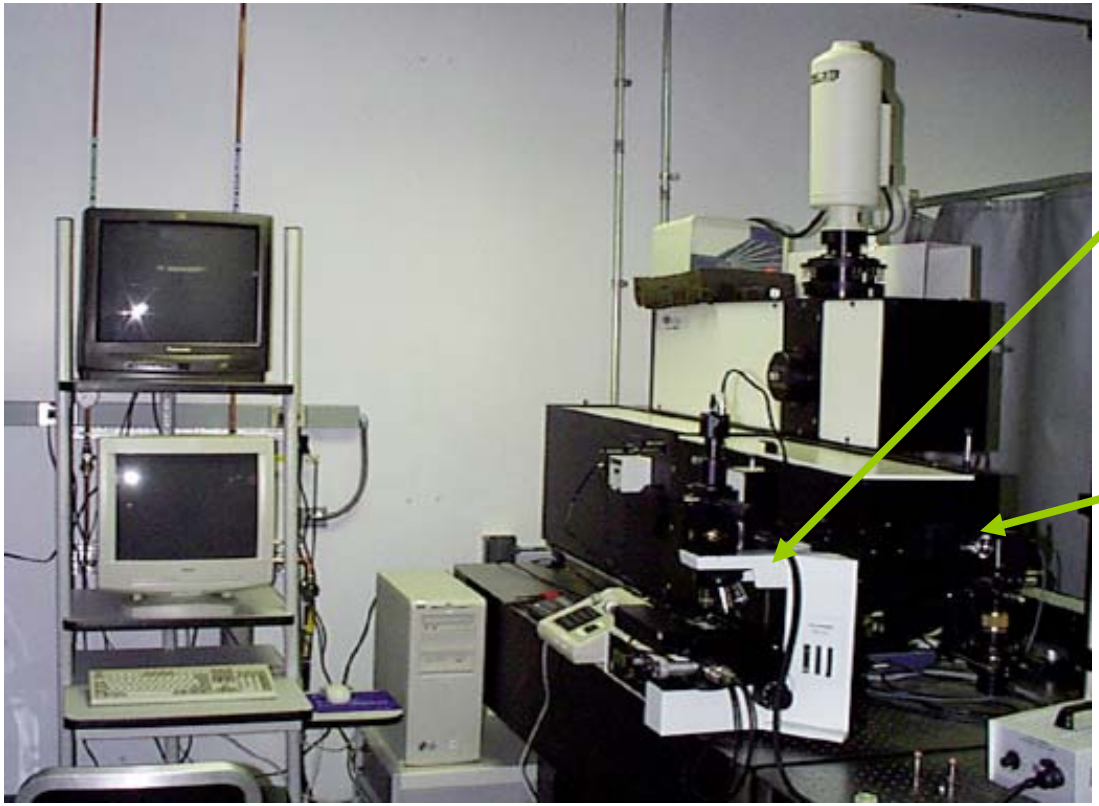


The Stokes/anti-Stokes Spectrum of Tetragonal Zirconia



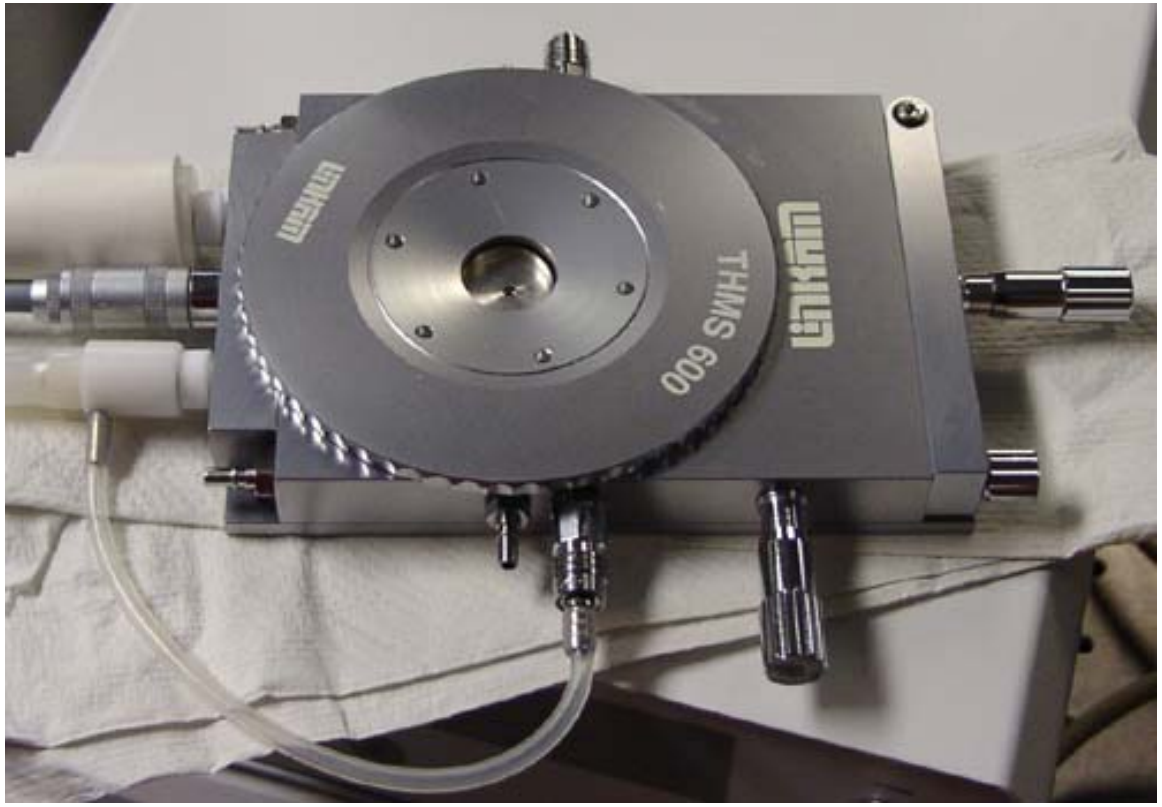
- Monochromatic (laser) light may create or destroy a vibration (phonon) through the Raman effect.
- Raman measures vibrations and so is sensitive to small changes in the structure or shape of gases caused by residing in different clathrate structures.

Dilor XY800 Raman Microprobe System



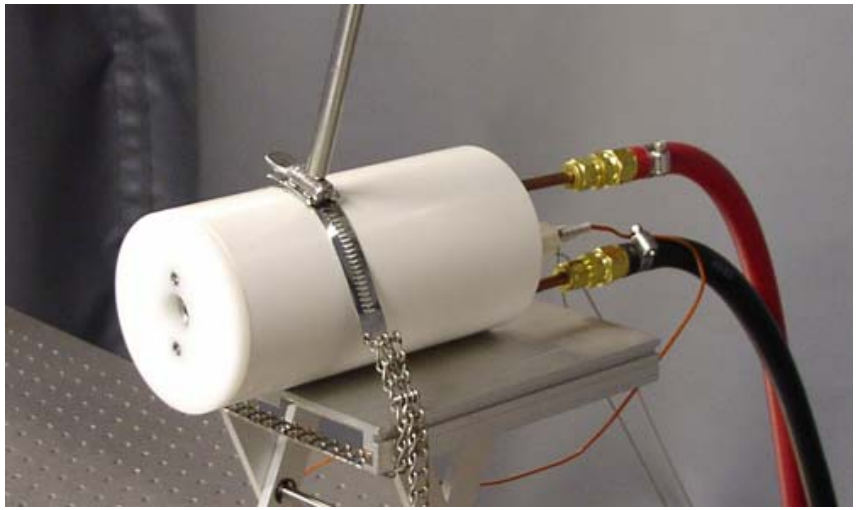
- **Spatial resolution of ~2 µm and depth resolution of ~5 µm.**
- **Microscope cooling stage down to -196°C.**
- **Confocal line imaging for 2D mapping.**
- **Diamond anvil cell reaching up to 5 GPa at room temperature.**
- **Macro stage and fiber optics for *in situ* measurement in pressure cells.**

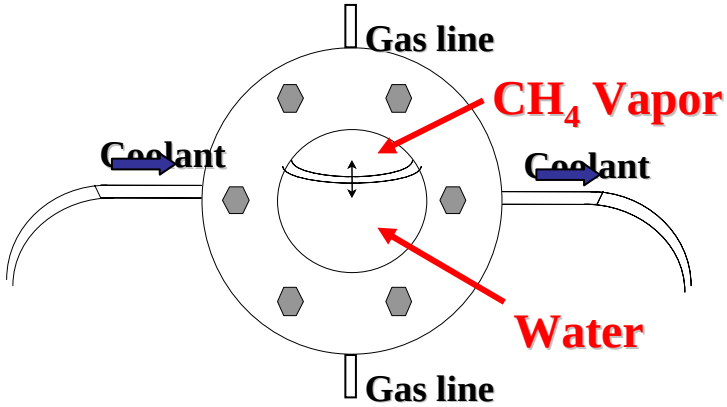
Linkham Low Temperature Stage

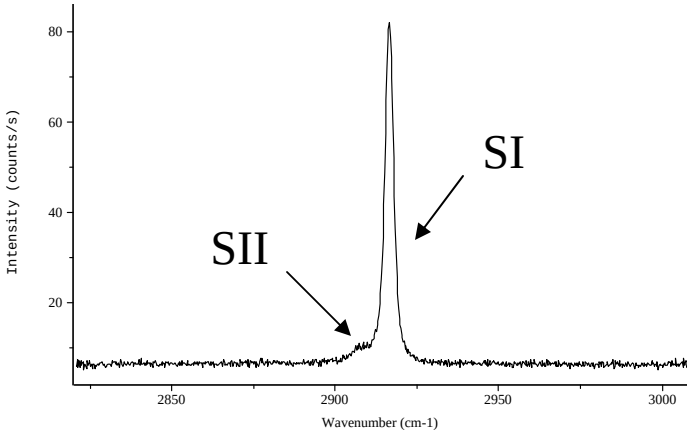


- Cooling down to 77K.
- Designed to be used with the microscope allowing for the measurement of microstructural effects in natural hydrate samples.

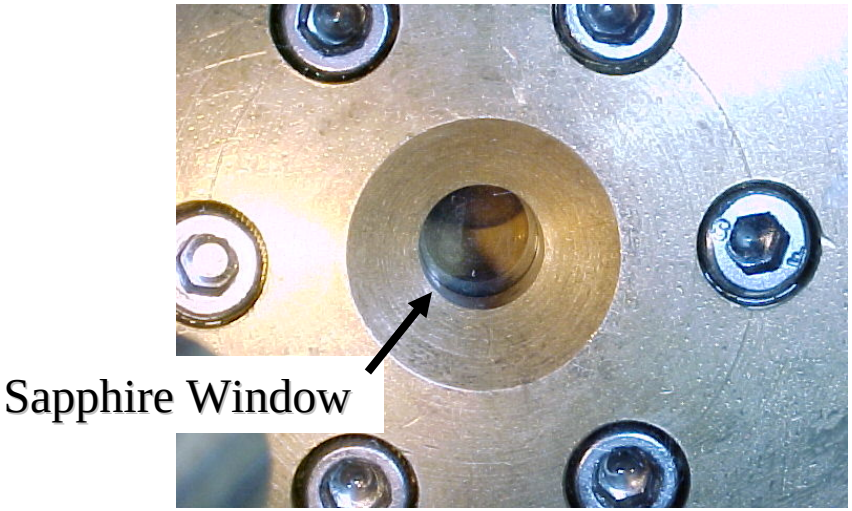
High Pressure Cell





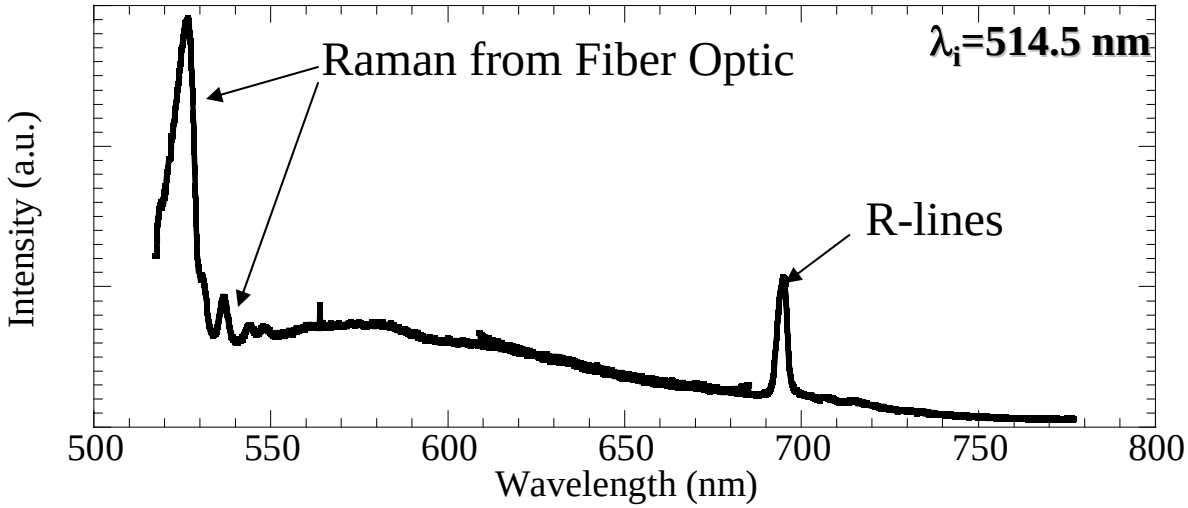


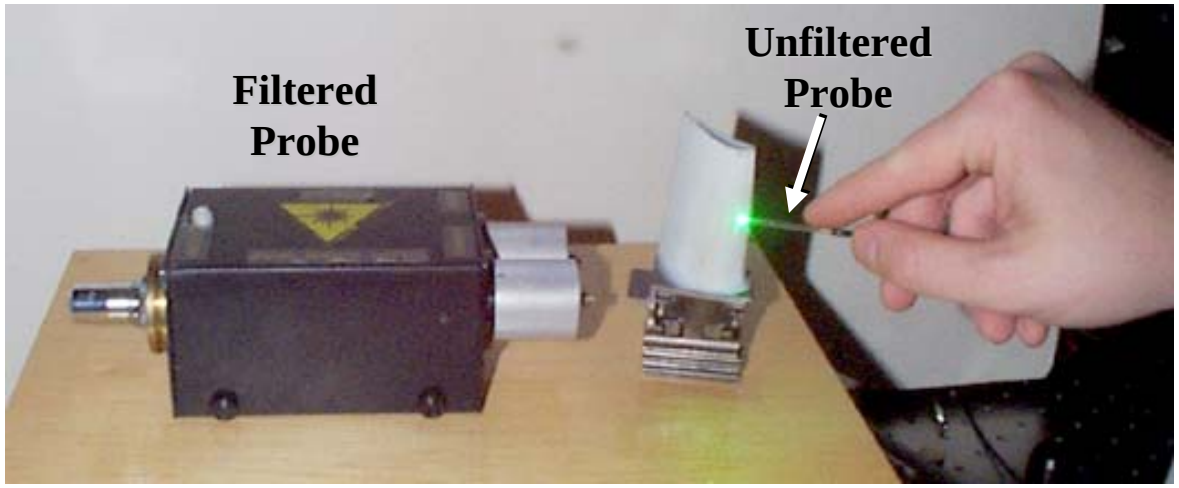
Pressure Cell Face



- The cell has a maximum pressure of 10,000 psi at 25ºC and can be cooled to -20ºC.
- A thermocouple inside the cell measures the temperature and a magnetic stirrer ensures a well-mixed solution.
- The initial test showed that we successfully created the methane hydrate at 5100 psi and 4ºC.

Remote Measurement using Fiber Optics





- Since the technique works in the visible range of the E-M spectrum, fiber optics can be used for remote sampling.
- The optical fiber will generate Raman peaks which must be filtered.
- This allows for in situ testing and even deep sea Raman measurements at MBARI.

Portable Raman System

- New portable Raman systems can be transported to different sites for rapid hydrate characterization.

“Raman spectroscopic studies on structure I and structure II trimethylene oxide hydrate”

Fig. 1. Overlay of Raman spectra of C–H stretching modes in the 2850–3050 cm^{-1} interval: (A), aqueous TMO; (B), pure TMO liquid; (C), TMO structure I clathrate hydrate; and (D), TMO solid at 150 K.

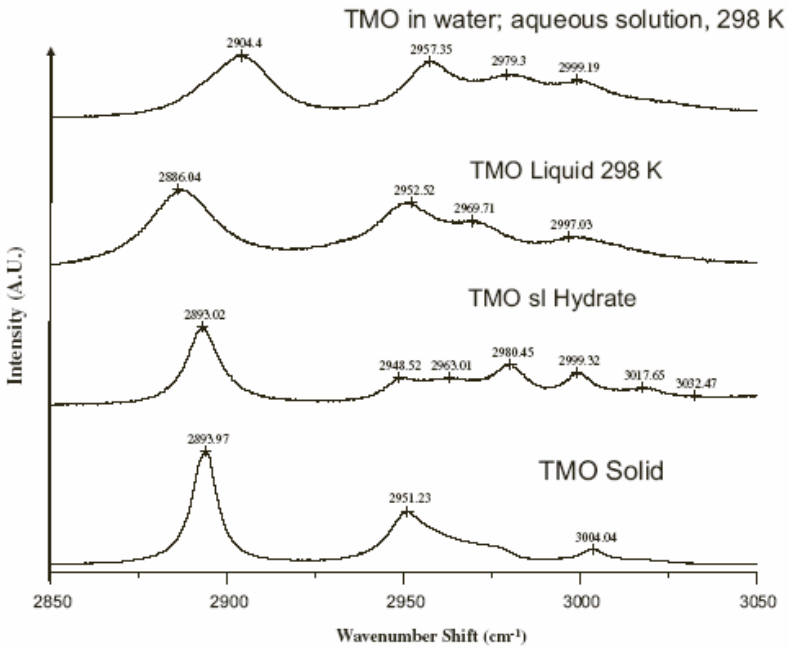
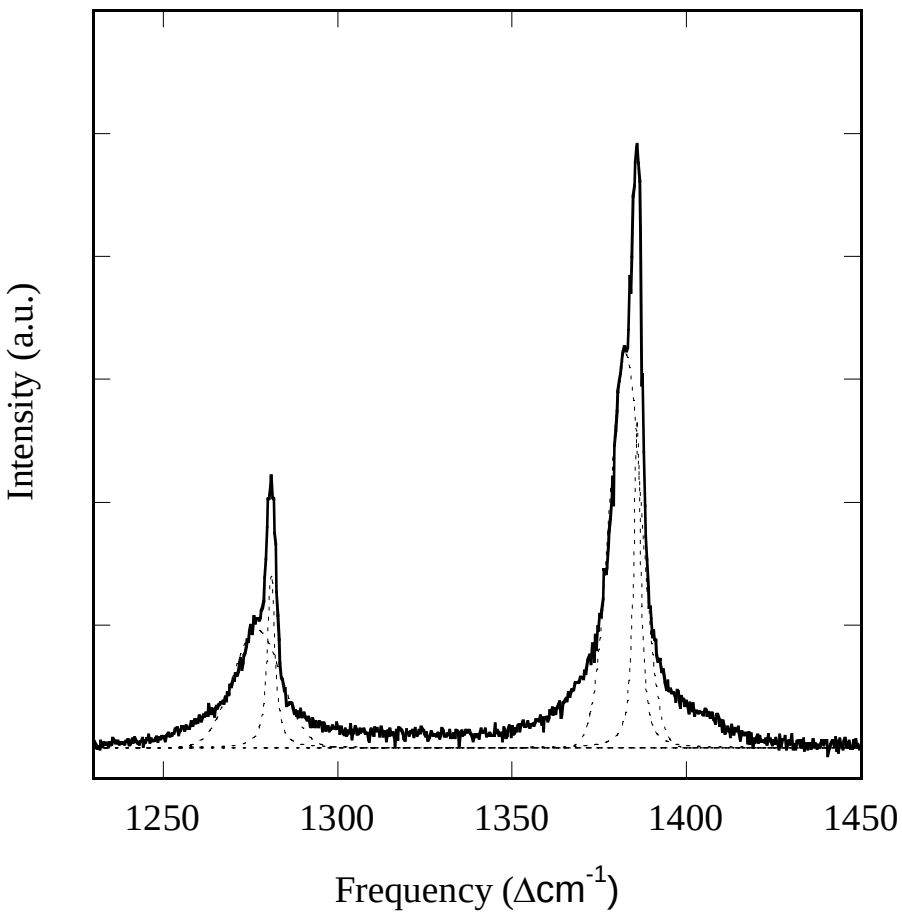


Table 2. Observed peak positions of liquid TMO and TMO sI hydrate, and a shift in frequency of the TMO hydrate relative to the observed frequencies of liquid TMO.

TMO liquid, (cm^{-1})	TMO-hydrate sI, $5^{12}6^2$, (cm^{-1})	Shift in frequency (cm^{-1})	Vibrational modes
2997.0 (m)	2999.3(m)	+2.3	$-CH_2(\beta)$ symmetric stretch
2969.7(sh)	2980.5(s)	+10.7	$-CH_2$ (β) asymmetric stretch
2952.5(s)	2948.5(m-w)	−4.0	$-CH_2$ (α) asymmetric stretch
2886.0(vs)	2893.0(vs)	+7.0	$-CH_2$ (α) symmetric stretch
1498.5(w)	1499.3(w)	+0.9	$-CH_2$ (α) symmetric scissor
1453.5(w)	1458.9(w)	+5.4	$-CH_2$ (β) asymmetric scissor
1338.0(vw)	1340.4(vw)	+2.4	$-CH_2$ (α) symmetric wag
1286.5(vw)	1284.1(vw)	−2.4	$-CH_2$ (β) asymmetric wag
1183.8(w)	1188.3(w)	+4.5	$-CH_2$ (β) symmetric wag
1139.1(w)	1139.8(vw)	+0.7	$-CH_2$ (β) symmetric twist
1027.7(vs)	1036.0(vs)	+8.3	Skeletal/ring mode
978.4(w)	981.5(w)	+3.1	C—O—C stretch
930.7(vw)	947.4(vw)	+16.7	Skeletal/ring mode

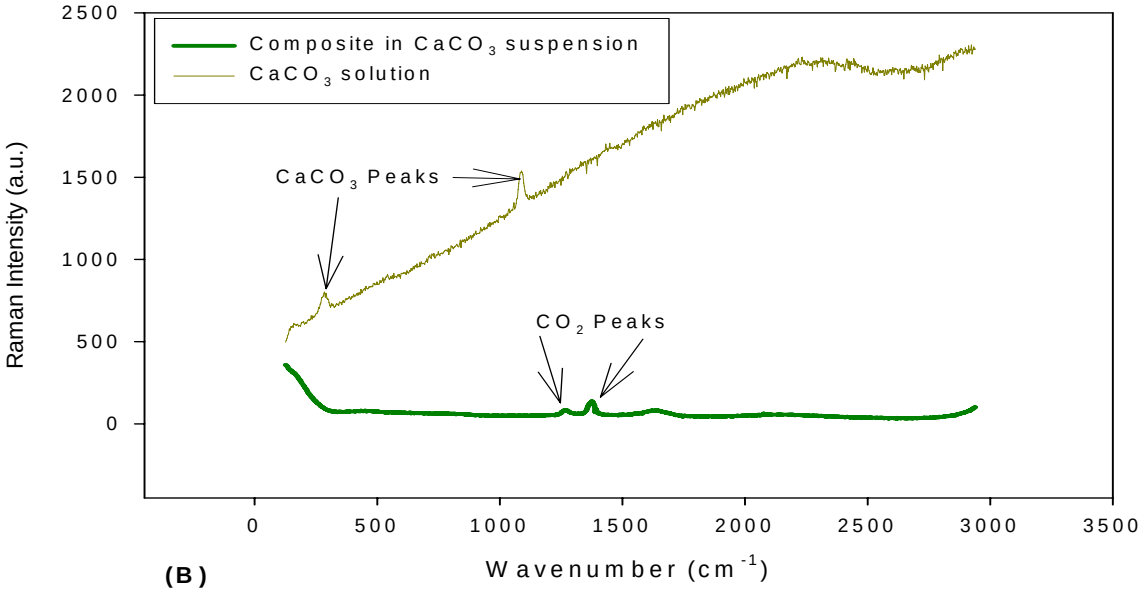
- The Raman peaks shift to higher frequencies when enclathrated.
- The “tight cage” of the water host lattice strains the TMO molecule causing the peak shift.

“Raman Spectroscopy of a Hydrated CO_2/Water Composite”



- Sharp bands are liquid CO_2 and the broad bands are from CO_2 hydrate.
- Hydration number couldn’t be measured due to large amount of water contained in the composite.
- However, the phase content of the composite could be estimated and used to determine how much CO_2 was lost to the surrounding water.

$CaCO_3$ Excluded from the Hydrate



- This suggests that salts will be excluded from the hydrate composite and will not effect hydrate conversion.

“Physical Properties of Gas Hydrate from Green Canyon, Gulf of Mexico”

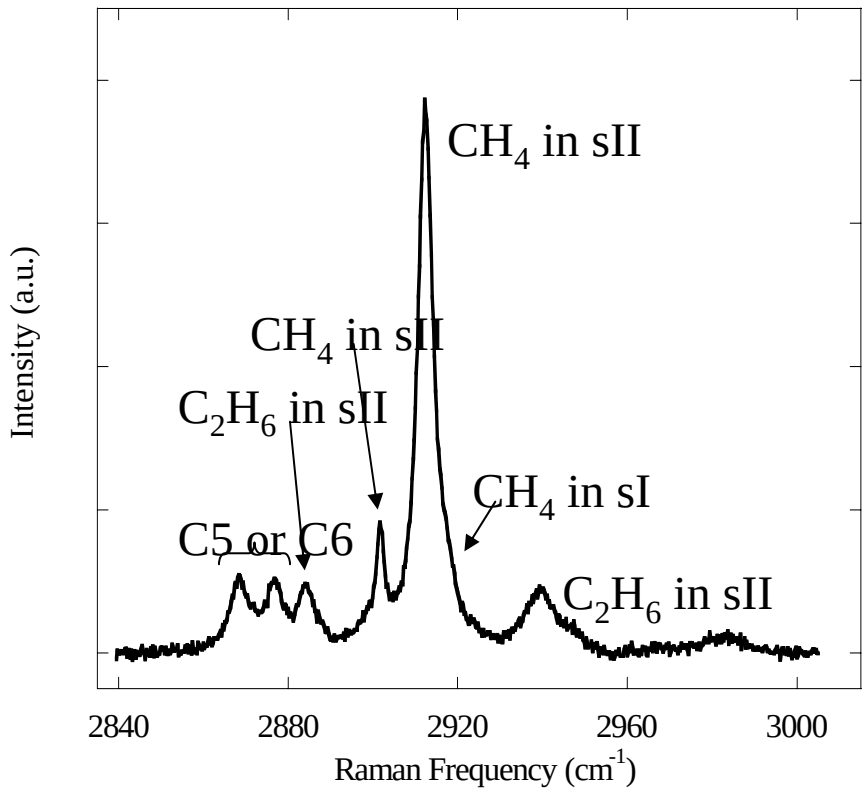


Table I: Assignment of Raman bands to different gas hydrates in natural samples.

Possible Clathrate 1st Guess	*Measured Peak Position (cm-1)*	*From Literature*
C5 or C6	2868.49	
C5 or C6	2876.71	
C2H6 in SII 5(12)6(2) Large	2884.34	2887.3
CH4 in SII 5(12)6(4) Large	2898.77	2903.72 +/- 0.28
CH4 in SI 5(12)6(2) Large	2901.73	2904.85 +/- 0.33
CH4 in SII 5(12) Small	2912.32	2913.73 +/- 0.76
CH4 in SI 5(12) Small	2917.14	2915.04 +/- 0.58
C2H6 in SII 5(12)6(2) Large	2939.47	2942.3
C2H6 in SI 5(12)6(2) Large	2947.46	2946.2
???	2982.53	

- Raman was used to identify different gas species in natural samples.