Raman spectroscopic data from gas hydrates formed from a complex gas mixture with different gas supply conditions

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1. Licence

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3. Data Description

Natural gas hydrates encase predominantly methane, but also higher hydrocarbons as well as CO_2 and H_2S. The formation of gas hydrates from a changing gas mixture, either due to the preferred incorporation of certain components into the hydrate phase or an inadequate gas supply, may lead to significant changes in the composition of the resulting hydrate phase. To determine the overall composition of a hydrate phase during the hydrate formation process, Raman spectroscopy is regarded as a non-destructive and powerful tool. This technique enables to distinguish between guest molecules in the free gas or liquid phase, encased into a clathrate cavity or dissolved in an aqueous phase, therefore providing time-resolved information about the guest molecules during the hydrate formation process.

Experiments were carried out at the Micro-Raman Spectroscopy Laboratory, GFZ. Mixed gas hydrates were synthesized in a high-pressure cell from pure water and a specific gas flow containing CH_4, C_2H_6, C_3H_8, iso-C_4H_{10} and n-C_4H_{10} at 274 K and 2.20 MPa. Three potential different gas supply conditions were selected for the formation of mixed gas hydrates, namely an open system (test scenario 1) with a continuous gas supply, a closed system (test scenario 2) with no gas supply after initial pressurization with the gas mixture, and a semi-closed system (test scenario 3) with only an incoming gas but a disrupted outlet. *In situ* Raman spectroscopic measurements and microscopic observations were applied to record changes in both gas and hydrate compositions over the whole formation period until it reached a steady state. In all three test scenarios, 12 hydrate crystals were selected and continuously characterized for 5 days with single point Raman measurements to record the formation process of mixed gas hydrates. Each test scenario was repeated for 3 times, therefore resulting in 9 separate experimental tests.

This dataset encompasses raw Raman spectra of the 9 experimental tests (.txt files) which contained Raman shifts and the respective measured intensities. Each Raman spectrum was fitted to Gauss/Lorentz function after an appropriate background correction to estimate the band areas and positions (Raman shift). The Raman band areas were then corrected with wavelength-independent cross-sections factors for each specific component. The concentration of each guest molecule in the hydrate phase / gas phase was given as mol% in a separate spreadsheet for three different test scenarios. Further details on the analytical setup, experimental procedures and composition calculation are provided in the following sections.

3.1. Sampling method

Mixed gas hydrates were synthesized in a custom-made pressure cell in the laboratory from water and a certified gas mixture containing CH_4, C_2H_6, C_3H_8, iso-C_4H_{10}, and n-C_4H_{10}. Initially, the sample cell was filled with 150 µl deionized and degassed water, carefully sealed and pressurized with the respective gas mixture. When the pressure reached 2.20 MPa and the flowrate was constant, the cell was cooled down to 253 K to induce the spontaneous crystallization of hydrate and ice. After the formation of hydrates and ice, the cell was slowly warmed up to allow the dissociation of ice and most hydrate crystals until only a few hydrate crystals were left. Subsequently, the cell was cooled down again to a temperature within the stability field of the hydrate phase, but above the melting temperature of the ice. Under these conditions set, euhedral gas hydrate crystals were allowed to grow. This “melting-cooling” process was carried out three times before the p-T condition was fixed at 2.20 MPa and 274 K for the formation of mixed gas hydrates.

To investigate the hydrate formation process, three different test scenarios were carried out with different gas flows but under identical p-T conditions. The inlet and outlet valves located outside the pressure cell were set to the desired position once the mixed gas hydrates started to form. In test scenario 1 (open system), the inlet and outlet valves were kept open throughout the whole experiment. Test scenario 2 (closed system) was carried out with the inlet and outlet valves being closed right after initial pressurization to mimic a system with a limited gas supply. The outlet valve was closed in test scenario 3 (semi-closed system) while the inlet valve was open. These changes on the gas flow were maintained throughout the whole formation process. Each test scenario was repeated for 3 times during the experiments.

3.2. Analytical procedure

A confocal Raman spectrometer (LABRAM HR Evolution, Horiba Jobin Yvon) with 1800-grooves/mm grating and a 20× microscope Olympus BX-FM objective was used for the *in situ* Raman measurements on the mixed gas hydrates. The excitation source was a frequency-doubled Nd:YAG solid-state laser with an output power of 100 mW working at 532 nm. With a focal length of 800 mm, the spectral resolution reached around 0.6 cm^{-1}. A motorized pinhole in the analyzing beam path enabled to variably increase the spatial resolution of laser-spot measurements which in x-y-direction was 0.5 µm and 1.5 µm in z-direction. Before the experiments, the Silicon band (521 cm^{-1}) was employed for the calibration of Raman band positions. During the experiments, a pinhole size of 50 µm was chosen for measurements on the hydrate surface while a pin hole size of 100 µm was set for the gas phase measurements. The acquisition time was 5 seconds with 2 averaged exposures. Neutral density filters that adjusted the output laser power was selected at 100% for the experiment since it provided the best signal-to-noise ratio while laser irradiation damage at the sample was not observed.

For each experimental test, 12 hydrate crystals were randomly selected in the pressure cell. With the help of a motorized, software controlled Märzhauser Scan+ sample stage attached to the microscope, which allowed for the positioning of the sample cell at defined coordinates, the selected hydrate crystals could be monitored over the entire duration of the experiment. Single point Raman spectroscopic measurements were performed right after initial pressurization on hydrate crystal surface. For the following 4 days, a continuous characterization on these crystals were carried out to record the changes of hydrate composition during the formation process.

3.3. Data processing

For the determination of the band areas in the Raman spectra, the software package Labspec 6.5 was used. Each raw spectrum was automatically fitted to Gauss/Lorentz function after an appropriate background correction to estimate the band areas and positions (Raman shift). The results were manually checked for integrity (no spurious peaks, convergence of multiple runs, no strong fluorescence) so that all the fittings were with sufficient quality for further evaluation and calculation. After determination of the peak area from the spectra, this area was corrected with a wavelength-independent cross-section factor (σ) of the respective gas component to determine a semi-quantitative composition of the sample, assuming that the cross-section factor did not vary with pressure, cage type, or the overall composition of the phases (Burke, 2001; Schrader, 1995; Schrötter & Klöckner, 1979).

Raman band areas of the components in a mixed system were proportional to the number of molecules present in the sample, thus the composition of the mixed hydrate phase was calculated by integrating the Raman band intensities to determine the area for each component. The molar composition of each

component in the gas and hydrate phase was given as relative percentage (mol%) assuming that the total Raman bands for the guest molecules were set to 100%.

4. File description

4.1. File inventory

The data are organized in the following folder structure:

- 2021-003_Pan-and-Schicks_Open-system
  - 2021-003_Pan-and-Schicks_Test-1_open
  - 2021-003_Pan-and-Schicks_Test-2_open
  - 2021-003_Pan-and-Schicks_Test-3_open
    - Individual folders are named after the measuring date (e.g. 20190909 means that the folder contains all the Raman spectral data taken on 9th September, 2019 in an open system)
      - Individual .txt file for each measured Raman spectrum, with the file name composed of either “hydrate crystal number_measuring time” or “gas phase_measuring time” (e.g. p1_1139 represents crystal 1 measured on 11:39). In each .txt file, the first column gives the Raman shift (in cm^-1) while the second column give the respective measured intensity (in arbitratry units).
- 2021-003_Pan-and-Schicks_Closed-system
  - 2021-003_Pan-and-Schicks_Test-1_closed
  - 2021-003_Pan-and-Schicks_Test-2_closed
  - 2021-003_Pan-and-Schicks_Test-3_closed
    - Individual folders are named after the measuring date (e.g. 20200210 means that the folder contains all the Raman spectra data taken on 10th February, 2020 in a closed system)
      - Individual .txt file for each measured Raman spectrum, with the file name composed of either “hydrate crystal number_measuring time” or “gas phase_measuring time” (e.g. p1_1337 represents crystal 1 measured on 13:37). In each .txt file, the first column gives the Raman shift (in cm^-1) while the second column give the respective measured intensity (in arbitratry units).
- 2021-003_Pan-and-Schicks_Semi-closed-system
  - 2021-003_Pan-and-Schicks_Test-1_semi-closed
  - 2021-003_Pan-and-Schicks_Test-2_semi-closed
  - 2021-003_Pan-and-Schicks_Test-3_semi-closed
    - Individual folders are named after the measuring date (e.g. 20200511 means that the folder contains all the Raman spectra data taken on 11th May, 2020 in a semi-closed system)
      - Individual .txt file for each measured Raman spectrum, with the file name composed of either “hydrate crystal number_measuring time” or “gas phase_measuring time” (e.g. p1_1255 represents crystal 1 measured on 12:55). In each .txt file, the first column gives the Raman shift (in cm^-1) while the second column give the respective measured intensity (in arbitratry units).
- 2021-003_Pan-and-Schicks_Composition-results

- 2021-003_Pan-and-Schicks_Composition-results.xlsx: contains 9 spreadsheets. Each spreadsheet provides the calculated hydrate composition (and gas composition) during the formation process from one experimental test.
- All 9 spreadsheets are also available as tab-delimited text files. Special characters σ and Δ used in the excel file have been written out to sigma and delta, respectively.

4.2. Description of data tables

The file 2021-003_Pan-and-Schicks_Composition-results.xlsx contains results of calculated composition of the hydrate phase and gas phase during the hydrate formation process under three gas supply conditions. Blank fields have been substituted by 'NA' values.

Column header	unit	Description
Date	yyyy-mm-dd	Date of measurement
Time	hh-mm-ss	Time of measurement
Crystal number		Hydrate crystal identifier
Raman shift	cm^-1	Raman band positions provided by the software package Labspec 6.5
Width	cm^-1	Full width at half maximum of the Raman band
Area	arbitratry units	Raman band areas provided by the software package Labspec 6.5
Corrected Raman band area	arbitratry units	Raman band area after correction with the respective Raman scattering cross-section factor for each gas component
Hydrate composition (mol %)	mol %	Relative composition of the hydrate phase calculated from the corrected Raman band areas
Gas composition (mol %)	mol %	Relative composition of the gas phase calculated from the corrected Raman band areas
Absolute pressure in the pressure cell (bar)	bar	Real-time absolute pressure in the closed system
△time (mins)	minutes	Time difference between the measuring time and the initial *t*=0 when the experiments first started
Molecule		Each specific gas component
σ	$(cm^2/sr) \times 10^{-30}$	Raman scattering cross-section factor

5. References

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