Geophysical Research Abstracts
Vol. 12, EGU2010-5367-1, 2010
EGU General Assembly 2010

Natural and synthetic gas hydrates studied by Raman spectroscopy

Jean-Philippe Savy, Nikolaus Bigalke, Giovanni Aloisi, Elke Kossel, Moritz Pansegrau, and Matthias Haeckel
Leibniz Institute for Marine Sciences (IFM-GEOMAR) , Kiel, Germany. jsavy@ifm-geomar.de

Over the past decade, the interest in using CH_4-hydrates as an energy resource and CO_2-hydrates as a storage option for anthropogenic CO_2 has grown in the scientific community as well as in the oil and gas industry. Among all the techniques used to characterize gas hydrates, the non-destructive, non-invasive Raman spectroscopy provides significant insights into the structure and composition of hydrates.

In this study, we compare gas hydrates synthetically produced in the laboratory with natural hydrate samples collected from marine sediments. CO_2 and CH_4 gas hydrates were investigated with a high-resolution Raman microscope at in-situ p-T conditions. A water-filled glass capillary (inner diameter: 1.7 mm) was placed in a stainless steel cell, which was sealed, cooled down to 3.6 ˚C and pressurized to 60 bar with liquid CO_2. Video images taken after 1 h revealed droplets ($\sim$10 μm in diameter) trapped in the ice-like solid. The two Fermi dyads of CO_2 in the liquid and hydrate phase at 1274 & 1381 cm^1 and 1280 & 1384 cm^{-1}, respectively, confirm the presence of liquid CO_2 droplets trapped in a CO_2-hydrate matrix.

Equivalent experiments were conducted with CH_4 gas at 1 ˚C and 90 bar. The nucleation of CH_4-hydrate was followed in the Raman spectral region of the C-H stretching mode. At the early stage of the nucleation, the peak at 2915 cm^{-1} (CH_4 in small cages) was stronger than the one at 2904 cm^{-1} (CH_4 in large cages) indicating that methane starts to populate the small 5^{12} cages of the s-I hydrate structure first and then, as nucleation continues, the large cages are stabilized leading to a quickly growing peak at 2904 cm^{-1} until a final peak intensity ratio of 3.7 is established. In contrast to other studies, intermediate stabilization of the s-II structure was not observed. Video images confirmed the absence of gas inclusions. The hydrate density, 1.1 & 0.9 for CO_2-hydrate and CH_4-hydrate respectively, compared to the one of water may explain the formation of inclusions during the crystallization of hydrates.

Finally, we investigated a natural CH_4 hydrate sample collected from Hikurangi Margin, New Zealand. Areal mapping of the sample revealed a constant peak area ratio of 3.7 between large and small cages, identical to our synthetic CH_4-hydrate. We also used the relative Raman signal intensities between CH_4 and H_2O to quantify the spatial variation in cage occupancy and methane concentration in the natural hydrate sample. Compared to synthetic CH_4-hydrate, the natural sample shows an inhomogeneous overall distribution of methane content.