Raman spectroscopic analysis of mixed-gas (methane and hydrogen sulfide) hydrate

Keito Kakizaki[1], *Akihiro Hachikubo[1], Satoshi Takeya[2]

1. Kitami Institute of Technology, 2. National Institute of Advanced Industrial Science and Technology (AIST)

Natural gas hydrates in subsurface marine sediment encage hydrogen sulfide. Microbial community produces hydrogen sulfide from methane ascending from deeper sediment layer and sulfate supplied from sea water. The existence of hydrogen sulfide decreases the equilibrium pressure of natural gas hydrate. Therefore, near-surface gas hydrates might exist in shallower area (i.e. less than 300m below sea level). On the other hand, hydration number decides the amount of gas in an unit volume/weight of crystal. In the case of ideal full-occupation of hydrate cages, the value of hydration number is 5.75 (Sloan and Koh, 2008). However, actual hydration number is estimated to be around 6, because small amount of empty cages decrease the free energy and stabilize the crystal. The cage occupancies and the hydration numbers can be estimated from these Raman peak intensities using a statistical thermodynamic model (Sum et al., 1997); however, the effect of hydrogen sulfide on the estimation has not examined yet. In this study, we synthesized methane and hydrogen sulfide mixed-gas hydrate and obtained their Raman spectra.

The mixed-gas hydrates were synthesized in a pressure cell, and retrieved the crystals at the temperature of liquid nitrogen. Hydrate-bound and residual gases were also sampled and their gas compositions were determined using gas chromatograph. Raman spectra were obtained at 123 K in the range 2,800-3,000 cm-1 and 2,500-2,700 cm-1 for the C-H stretching peaks of methane and the S-H stretching peaks of hydrogen sulfide, respectively. The Raman peaks were fitted using a Voigt function to obtain the integrated intensities of the two peaks corresponding to methane and hydrogen sulfide encaged in the large and small cages of the cubic structure I.

The methane peak ratio of large to small cages first increased with the composition of hydrogen sulfide (up to several percent), and then decreased and converged with the number of 3.2. On the contrary, The hydrogen sulfide peak ratio distributed from 2.4 to 2.8, increased with the composition of hydrogen sulfide, and then converged with the number of 3.2. These results suggest that molecules of hydrogen sulfide prefer to be encaged in small cages, although the molecular diameter of hydrogen sulfide is larger than that of methane.

Sloan and Koh (2008) Clathrate Hydrates of Natural Gases, 3rd ed., CRC Press: Boca Raton, FL, USA

Sum et al. (1997) Measurement of clathrate hydrates via Raman spectroscopy. J Phys Chem B 101: 7371-7377.

Keywords: gas hydrate, hydrogen sulfide, Raman spectroscopic analysis

