# アイソトポログのメタンを包接するクラスレートハイドレートのラマン分光分析

# Raman spectroscopic analysis of isotopologue methane hydrates

*菊池 優樹[1]、松田 純平[1]、八久保 晶弘[1]、竹谷 敏[2]
*Yuki Kikuchi[1], Jumpei Matsuda[1], Akihiro Hachikubo[1], Satoshi Takeya[2]

1. 北見工業大学、2. 産業技術総合研究所
1. Kitami Institute of Technology, 2. National Institute of Advanced Industrial Science and Technology (AIST)

Raman spectroscopy is one of the useful tool to get information of gas hydrate crystals. Natural gas hydrates in submarine/sublacustrine sediment mainly encage methane. Methane molecule is composed of carbon and hydrogen, and three kinds of isotopologues, $^{12}CH_4$, $^{13}CH_4$, and $CH_3D$ exist in nature. Ozeki *et al.* (2018) first reported Raman spectra of $CH_3D$ and $CD_4$ hydrates and compared with $CH_4$ (mainly $^{12}CH_4$) hydrate. We report Raman spectra of $^{13}CH_4$ hydrate and summarize Raman spectra of isotopologue methane hydrates.

$^{13}CH_4$ hydrate sample was synthesized in a small pressure cell (volume: 5 mL). Fine ice powder (1g) was put in the pressure cell, and introduced appropriate amount of $^{13}CH_4$ (purity: 99.5%, Taiyo-Nissan). $^{13}CH_4$ hydrate was formed by melting the fine ice powder at the temperature of 273.2 K under high pressure of $^{13}CH_4$. We retrieved the hydrate sample at 77 K and its Raman spectra was obtained at 123 K in the range 2,500-3,300 $cm^{-1}$ using a Raman spectrometer (RMP-210, JASCO Corporation). The Raman peaks were fitted in the range 2,800-3,000 $cm^{-1}$ for the C-H stretching peaks of methane using a Voigt function to obtain the integrated intensities of the two peaks corresponding to methane encaged in the large and small cages of the cubic structure I.

Raman shifts for the C-H stretching and bending modes of $^{13}CH_4$ was 0.8 $cm^{-1}$ and 14 $cm^{-1}$ smaller than those of $^{12}CH_4$, respectively, suggesting that $^{13}C$-H bonds affect its vibrational frequency. Hydration number of $^{13}CH_4$ was estimated as 6.00±0.02, almost the same as that of $^{12}CH_4$ (6.02±0.02). Therefore, Cage occupancies of $^{13}CH_4$ and $^{12}CH_4$ hydrates showed no difference between them.

Reference

Ozeki T, Kikuchi Y, Takeya S, Hachikubo A (2018) Phase equilibrium of isotopologue methane hydrates enclathrated $CH_3D$ and $CD_4$. J Chem Eng Data 63(6): 2266-2270, doi: 0.1021/acs.jced.8b00203

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