Raman spectroscopic analysis of isotopologue methane hydrates

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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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