

## Effect of temperature on the C–H symmetric stretching vibrational frequencies of methane in structure H and I clathrate hydrates

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Clathrate hydrates are crystalline inclusion compounds that consist of guest molecules of suitable sizes and shapes trapped in well-defined cages formed by water molecules. Both synthetic and naturally occurring clathrate hydrates with natural gases as guest molecules are commonly known as gas hydrates. Gas hydrates with enclathrated hydrocarbon gases that exist in sea/lake bottom sediments and permafrost layers have attracted considerable interest as a potential source of unconventional natural gas.

Three typical crystal structures of clathrate hydrates have been identified on Earth: cubic structure I (sI), cubic structure II (sII), and hexagonal structure H (sH). Small guest molecules such as methane ( $\text{CH}_4$ ) or ethane form sI-type hydrates, whereas larger molecules like propane or 2-methylpropane ( $\text{C}_4\text{H}_{10}$ ) form sII hydrates. sH hydrates are obtained from even larger molecules, e.g., 2-methylbutane ( $\text{C}_5\text{H}_{12}$ ) or 2,2-dimethylbutane ( $\text{C}_6\text{H}_{14}$ ), in the presence of a help gas as  $\text{CH}_4$ . In this study, the Raman spectra of the C–H symmetric stretch region of  $\text{CH}_4$  enclathrated within various sH hydrates and structure I  $\text{CH}_4$  hydrates were analyzed in the temperature range of 83–183 K. Thermal expansions of these sH hydrate samples were also measured using powder X-ray diffraction. Symmetric stretch vibrational frequencies of  $\text{CH}_4$  in host water cages increased because of varying temperature, and the sizes of host water cages also increased; variation of  $\text{CH}_4$  in small cages was less than in larger cages. Comparing the variations of the C–H symmetric stretching frequencies of  $\text{CH}_4$  in gas hydrates with varying pressure and temperature, we suggest that the observed trend is caused by thermal vibrations of the  $\text{CH}_4$  molecule in water cages.

### Reference

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

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