Trend of effect of temperature on C–H symmetric stretching vibrational frequencies of hydrocarbon molecules in 12, 14 and 16-hedra cages of gas 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. Clathrate hydrates with natural gases as guest molecules are commonly known as gas hydrates. Gas hydrates with enclathrated hydrocarbon gases that exist in sea or lake bottom sediments and permafrost layers have attracted considerable interest as a potential source of unconventional natural gas.

There are three common crystallographic structures of hydrates, structure I (sI), structure II (sII), and structure H (sH). The unit cell of sI hydrates are composed of two pentagonal dodecahedral (5^{12}) and six tetrakaidecahedral ($5^{12}6^2$) water cages. The unit cell of sII hydrates are composed of sixteen 512 cages and eight hexakaidecahedral ($5^{12}6^4$) water cages. Small guest molecules such as methane (CH_4) or ethane (C_2H_6) form sI hydrates and larger molecules such as propane (C_3H_8) form sII hydrates.

In this study, we observed the variations of Raman shifts of C–H symmetric stretching vibrations of various hydrocarbons encaged in $5^{12,}$ $5^{12}6^2$ and $5^{12}6^4$ cages of sI and sII hydrates. By changing temperature, we investigated variations of Raman shifts of C–H symmetric stretching vibrations of guest hydrocarbons. It was revealed that the vibrations of guest hydrocarbons in smaller sI 51262 cages were greater than those in bigger sII 51264 cages. These results are inconsistent with our prediction in earlier study (Fuseya et al. 2018), that is, the volume of host water cages increases, and the variations of the Raman shifts of C–H symmetric stretching vibrations of guest hydrocarbon molecules in host water cages due to change temperature increase. Taking into account the facts obtained in this study and in our earlier study, we conclude that the temperature change of Raman shifts of C–H symmetric stretching vibrations is affected by geometric asymmetry of host water cages.

Reference

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

Fuseya *et al.* (2018) Effect of temperature and large guest molecules on the C–H symmetric stretching vibrational frequencies of methane in structure H and I clathrate hydrates. *RSC Adv.* **8**: 3237-3242. doi: 10.1039/c7ra12334e

Keywords: gas hydrate, Raman spectroscopy, powder X-ray diffraction, molecular vibrations

