

Supporting Information

Temperature effects on the C–H symmetric stretching vibrational frequencies of guest hydrocarbon molecules in 5¹², 5¹²6² and 5¹²6⁴ cages of sI and sII clathrate hydrates

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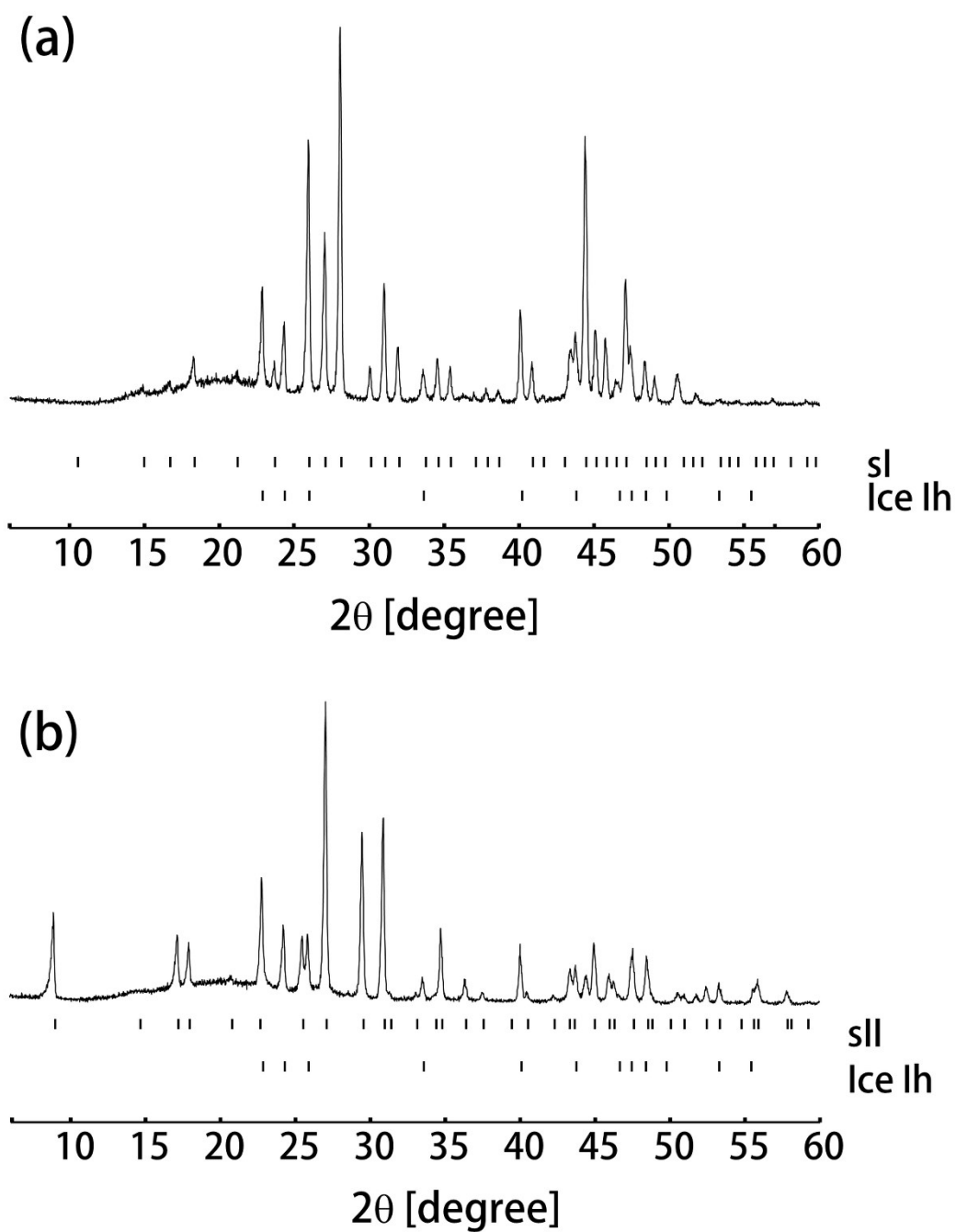


Fig. S1. X-ray diffraction patterns of the hydrate samples at 93 K: (a) sI C_2H_4 hydrate and (b) sII Kr + C_2H_4 hydrate. The curves in each pattern represent the observed intensities. The line marks below each pattern show the calculated peak positions for sI hydrate, sII hydrate and hexagonal ice.

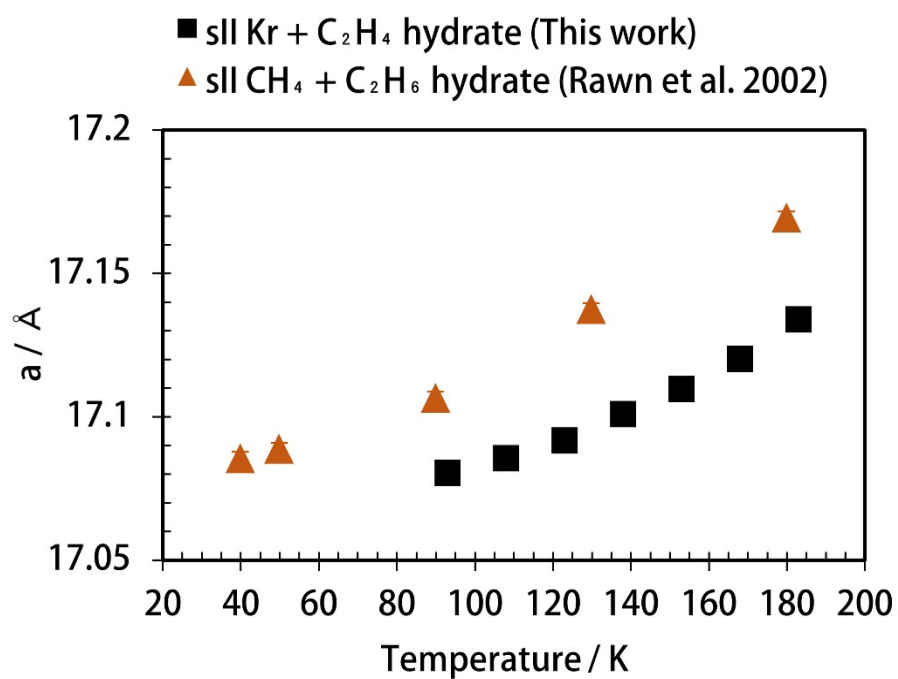
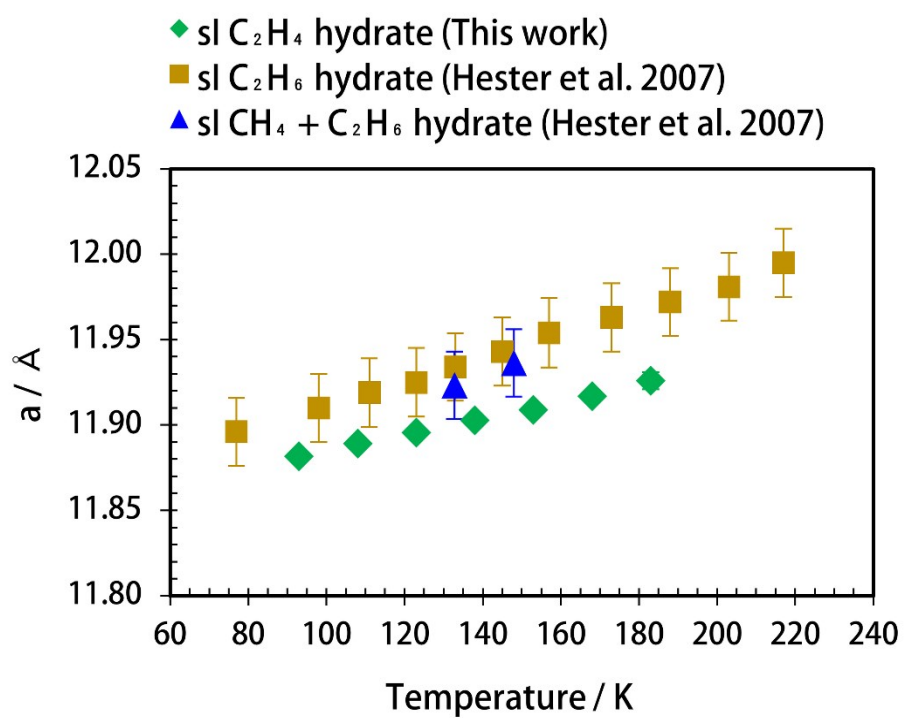


Fig. S2. Effect of temperature on unit-cell parameters of five types of sI and sII hydrates.^{1,2}

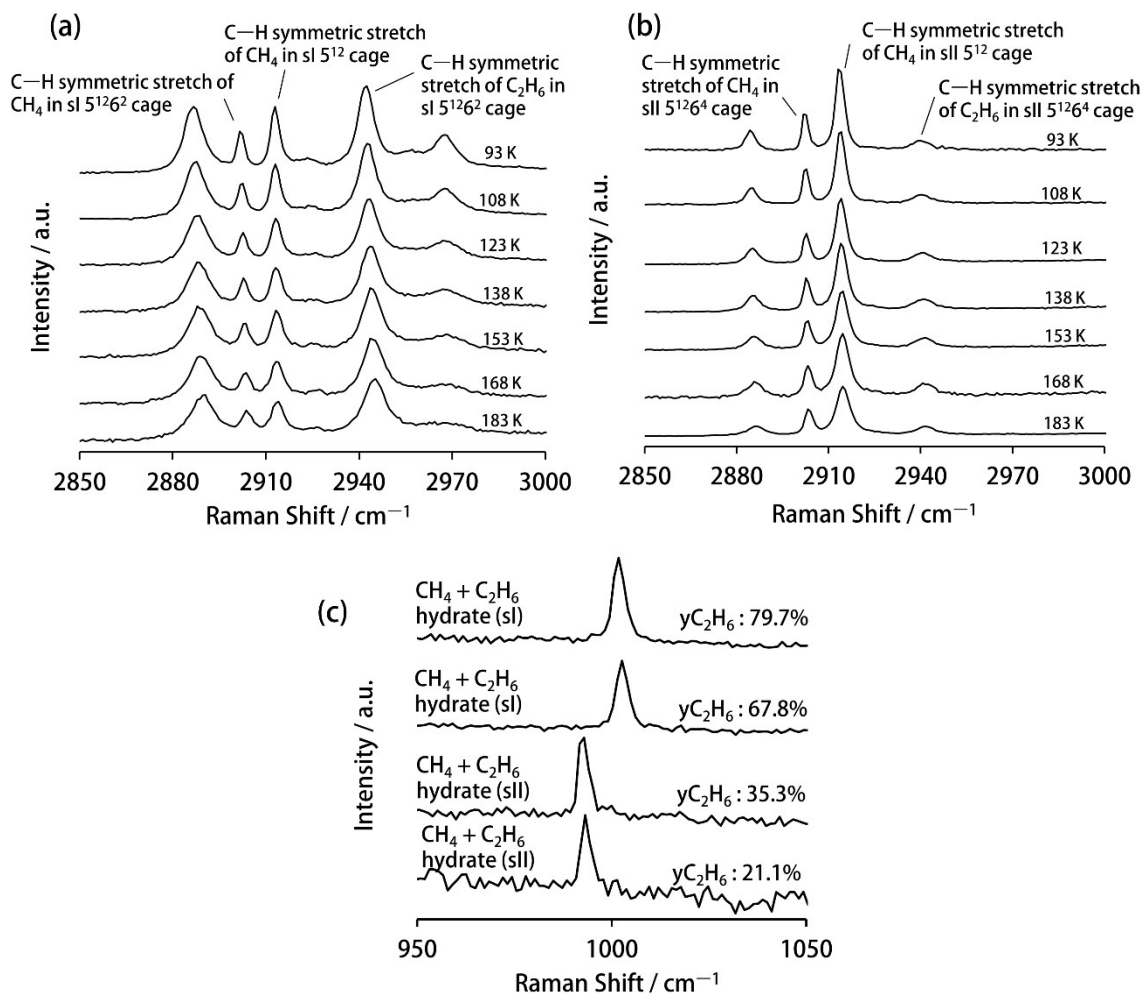


Fig. S3. Raman spectra of the C–H stretching region of (a) sI CH₄ + C₂H₆ hydrates (yC₂H₆ : 67.8%) and (b) sII CH₄ + C₂H₆ hydrates (yC₂H₆ : 21.1%) at a temperature range of 93–183 K. (c) Raman spectra of the C–C stretching region of encapsulated C₂H₆ in sI and sII CH₄ + C₂H₆ hydrates at 93 K.

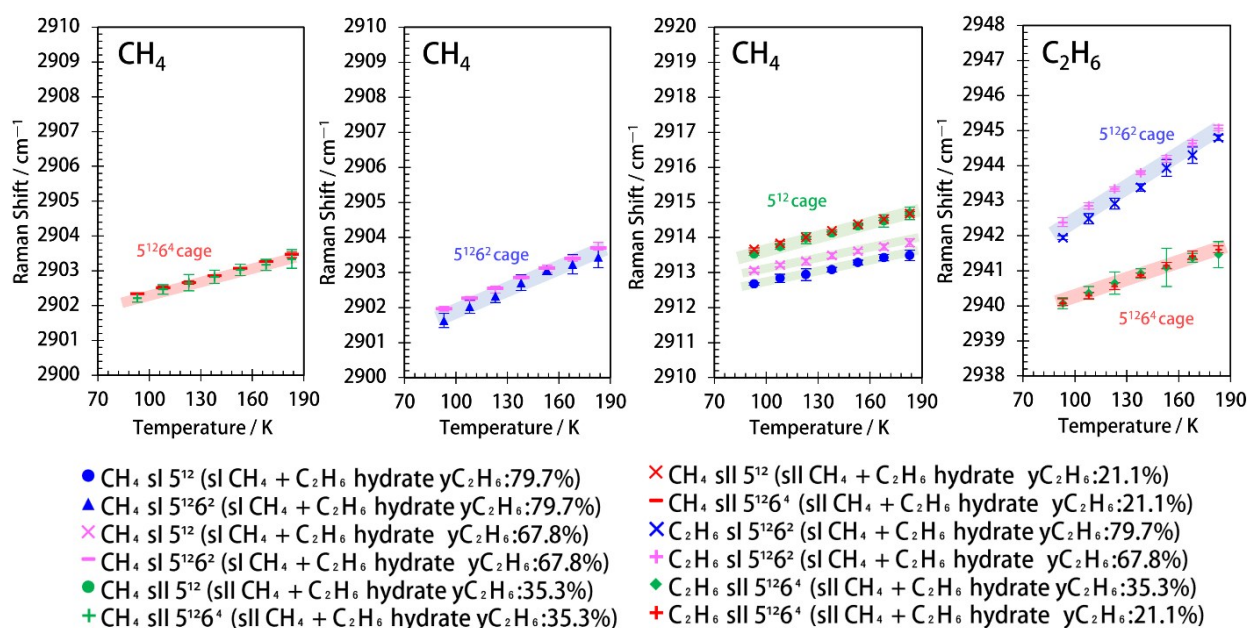


Fig. S4. Effect of temperature on Raman shifts of C–H symmetric stretch of encapsulated CH₄ and C₂H₆ in sl and slI CH₄ + C₂H₆ hydrates which have different guest composition.

Table S1 Raman shifts of C–H symmetric stretch of CH₄ and C₂H₆ in sI and sII CH₄ + C₂H₆ hydrates which have different guest composition and their variations with temperature changes. The errors are the standard deviations of nine measurements at different sample positions.

guest molecule	cage	structure	bulk guest composition of C ₂ H ₆ [%]	estimated cage occupancy ratio of CH ₄ in large cages ³	estimated cage occupancy ratio of C ₂ H ₆ in large cages ³	Raman shift at 93 K [cm ⁻¹]	slope of Raman shift between 93 K and 183 K ($\Delta\nu/\Delta T$) [10 ⁻² cm ⁻¹ /K]
CH ₄	5 ¹²	sI	79.7	0.04	0.94	2912.7 ± 0.1	+0.9 ± 0.1
	5 ¹² 6 ²	sI	79.7	0.04	0.94	2901.6 ± 0.1	+2.0 ± 0.3
	5 ¹²	sI	67.8	0.12	0.86	2913.1 ± 0.1	+0.9 ± 0.1
	5 ¹² 6 ²	sI	67.8	0.12	0.86	2902.0 ± 0.1	+1.9 ± 0.1
	5 ¹²	sII	35.3	0.14	0.83	2913.5 ± 0.1	+1.3 ± 0.2
	5 ¹² 6 ⁴	sII	35.3	0.14	0.83	2902.2 ± 0.1	+1.2 ± 0.1
	5 ¹²	sII	21.1	0.40	0.56	2913.7 ± 0.1	+1.2 ± 0.1
	5 ¹² 6 ⁴	sII	21.1	0.40	0.56	2902.3 ± 0.1	+1.3 ± 0.1
C ₂ H ₆	5 ¹² 6 ²	sI	79.7	0.04	0.94	2941.9 ± 0.1	+3.2 ± 0.1
	5 ¹² 6 ²	sI	67.8	0.12	0.86	2942.4 ± 0.1	+3.0 ± 0.1
	5 ¹² 6 ⁴	sII	35.3	0.14	0.83	2940.1 ± 0.1	+1.6 ± 0.1
	5 ¹² 6 ⁴	sII	21.1	0.40	0.56	2940.1 ± 0.1	+1.7 ± 0.1

References

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- [2] C. J. Rawn, A. J. Rondinone, B. C. Chakoumakos, S. L. Marshall, L. A. Stern, S. Circone, S. Kirby, C. Y. Jones, B. H. Toby, and Y. Ishii, Neutron Powder Diffraction Studies as a Function of Temperature of sII Hydrate Formed from a Methane + Ethane Gas Mixture. Proceedings of the 4th International Conference on Gas Hydrates, Yokohama, Japan, 2002.
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