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Nucleation and dissociation of methane clathrate embryo at the gas–water interface

Rongda Liang[a,1], Huijie Xu[a,1], Yuneng Shen[a], Shumei Sun[a], Jiyu Xu[b], Sheng Meng[b], Y. Ron Shen[a,c,2], and Chuanshan Tian (田传山)[a,d,2]

[a]Department of Physics, State Key Laboratory of Surface Physics and Key Laboratory of Micro- and Nano-Photonic Structure, Fudan University, 200433 Shanghai, China; [b]Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, 100190 Beijing, China; [c]Department of Physics, University of California, Berkeley, CA 94720; and [d]Collaborative Innovation Center of Advanced Microstructures, 210093 Nanjing, China

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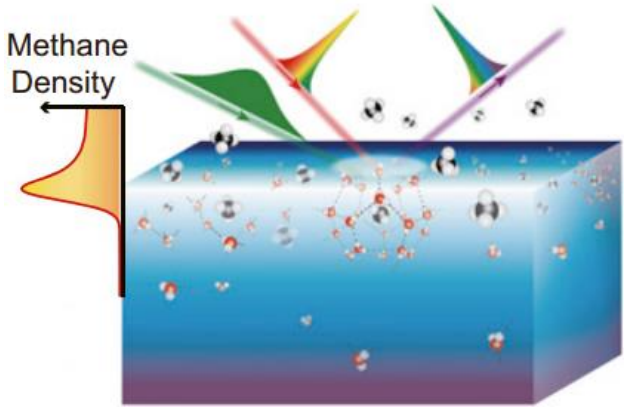
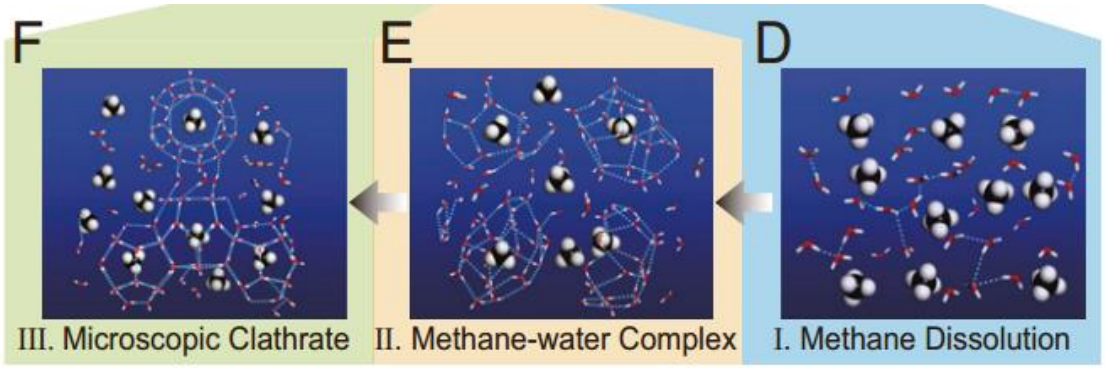
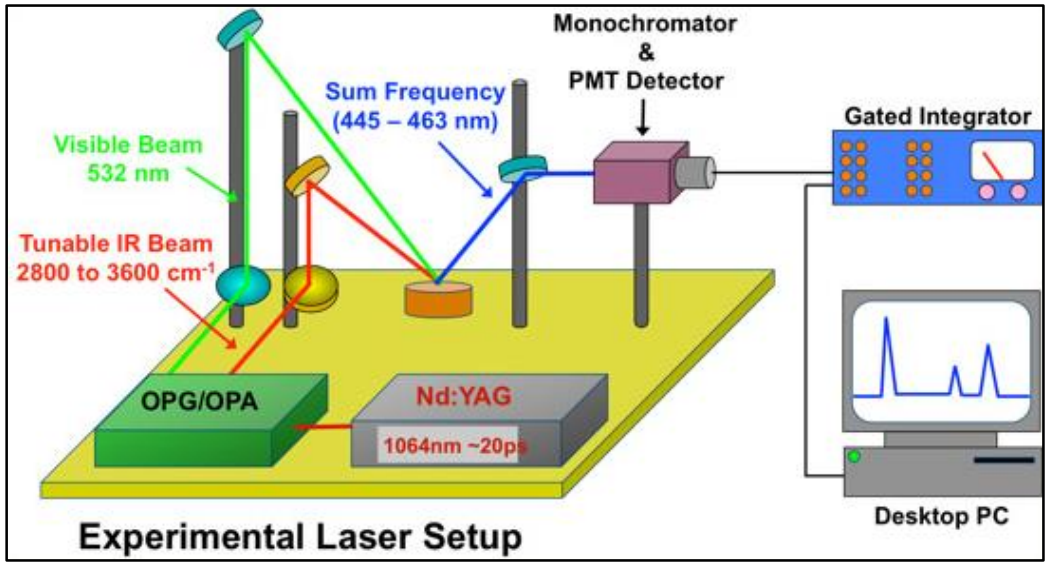


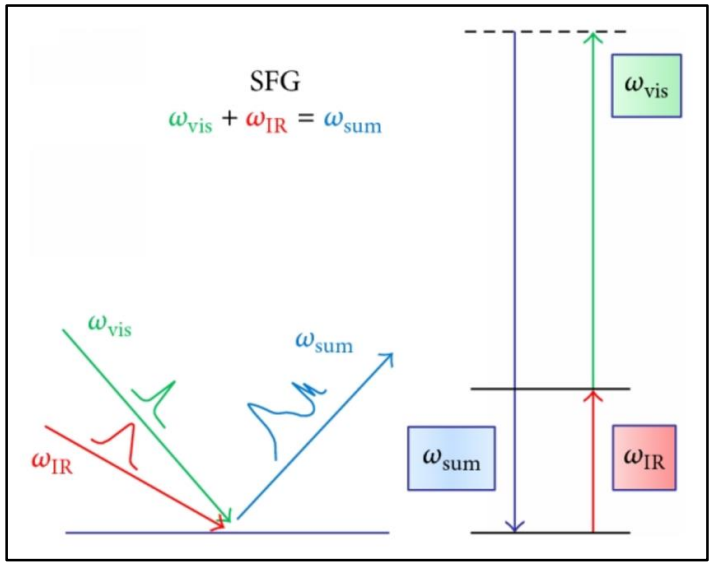


Jargon box

Embryo: something in an early stage of development

SFVS: sum-frequency vibrational spectroscopy





SFVS used to applied to deduce the composition, orientation distributions, and structural information of molecules at gas–solid, gas–liquid and liquid–solid interfaces.

https://www.hymarc.org/capabilities/sum-frequency-generation-vibrational-spectroscopy-sfg/

Background work

- E. D. Sloan, F. Fleyfel, A molecular mechanism for gas hydrate nucleation from ice. *AIChE J.* **37**, 1281–1292 (1991).
- R. L. Chris… *Ann. N. Y. Acad.* …
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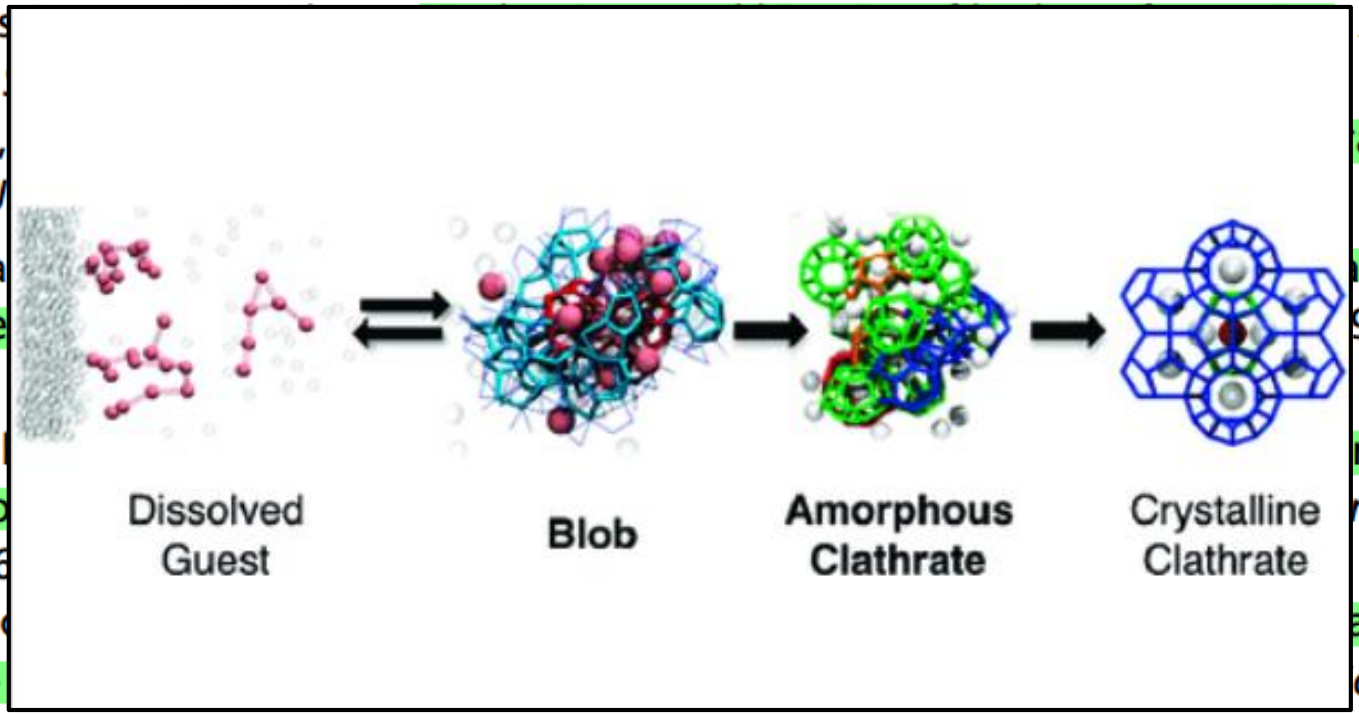
- B. C. Kn… …ation of methane … *oc.* **134**, 19544–19547 (2012).
- P. Pirzadeh, P. G. Kusalik, Molecular insights into clathrate hydrate nucleation at an ice-solution interface. *J. Am. Chem. Soc.* **135**, 7278–7287 (2013).



Jacobson, L. C. *et al.*, *J. Am. Chem. Soc.* **2010,** *132* (33), 11806-11811

Background work

ELSEVIER

Current Opinion in Solid State and Materials Science

Volume 20, Issue 6, December 2016, Pages 344-351

Some current challenges in clathrate hydrate science: Nucleation, decomposition and the memory effect

John A. Ripmeester [a] ✉, Saman Alavi [a, b]

THE JOURNAL OF CHEMICAL PHYSICS **145**, 211705 (2016)

Overview: Nucleation of clathrate hydrates

Pramod Warrier,[a)] M. Naveed Khan, Vishal Srivastava, C. Mark Maupin, and Carolyn A. Koh[a)]

Center for Hydrate Research, Chemical and Biological Engineering Department, Colorado School of Mines, Golden, Colorado 80401, USA

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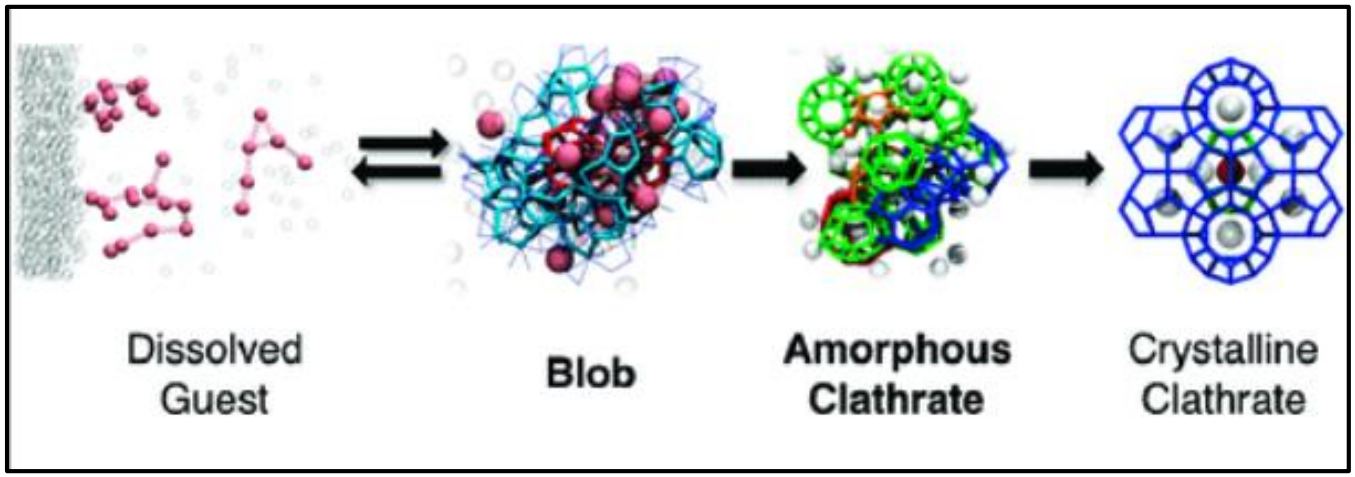
Molecular level knowledge of nucleation and growth of clathrate hydrates is of importance for advancing fundamental understanding on the nature of water and hydrophobic hydrate formers, and their interactions that result in the formation of ice-like solids at temperatures higher than the ice-point. The stochastic nature and the inability to probe the small length and time scales associated with the nucle-

Motivation

➡ How the clathrate starts to nucleate and disintegrate at the molecular level.

➡ According to molecular-dynamics (MD) simulations, after reaching a critical size, the clusters can transform first into amorphous and then into crystalline clathrate.



Why this paper?

- ➡ First experimental demonstration of clathrate hydrate nucleation process.
- ➡ Observation of clathrate nucleation with the help of surface sensitive SFVS.
- ➡ Experimental set-up

Introduction

- Among natural energy resources, methane clathrate has attracted particular attention for being the world's largest natural gas resources beneath permafrost and ocean sediments.

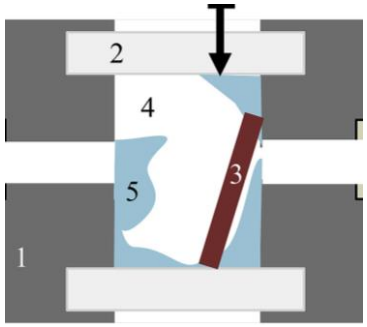
- Nucleation of clathrate is still a poorly understood process although its knowledge is crucial for control of clathrate formation and dissociation in many applications.

- Using surface-specific sum-frequency vibrational spectroscopy (SFVS), they have studied in situ the nucleation and disintegration of methane clathrate embryos at the methane-gas–water interface under high pressure and different temperatures.

- Before appearance of macroscopic methane clathrate, the interfacial structure undergoes 3 stages as temperature varies-
  1. dissolution of methane molecules into water interface,
  2. formation of cage-like methane–water complexes,
  3. appearance of microscopic methane clathrate, while the bulk water structure remains unchanged.

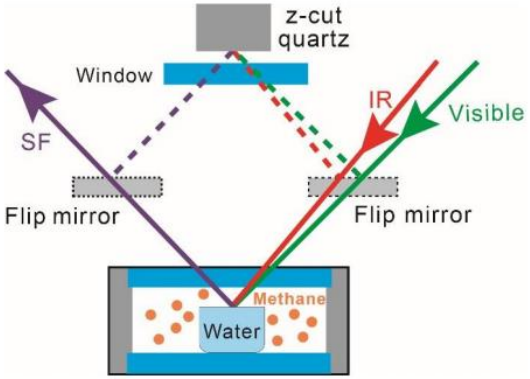
Experimental Methods

➡ **Preparation of Polycrystalline Methane Clathrate:** Deuterated water and methane were used for growth of methane clathrate in the high-pressure chamber at 5 °C, with the methane pressure at 4.0 MPa and water mildly perturbed by a Teflon-coated magnetic stirrer, growth of polycrystalline methane clathrate was observed.



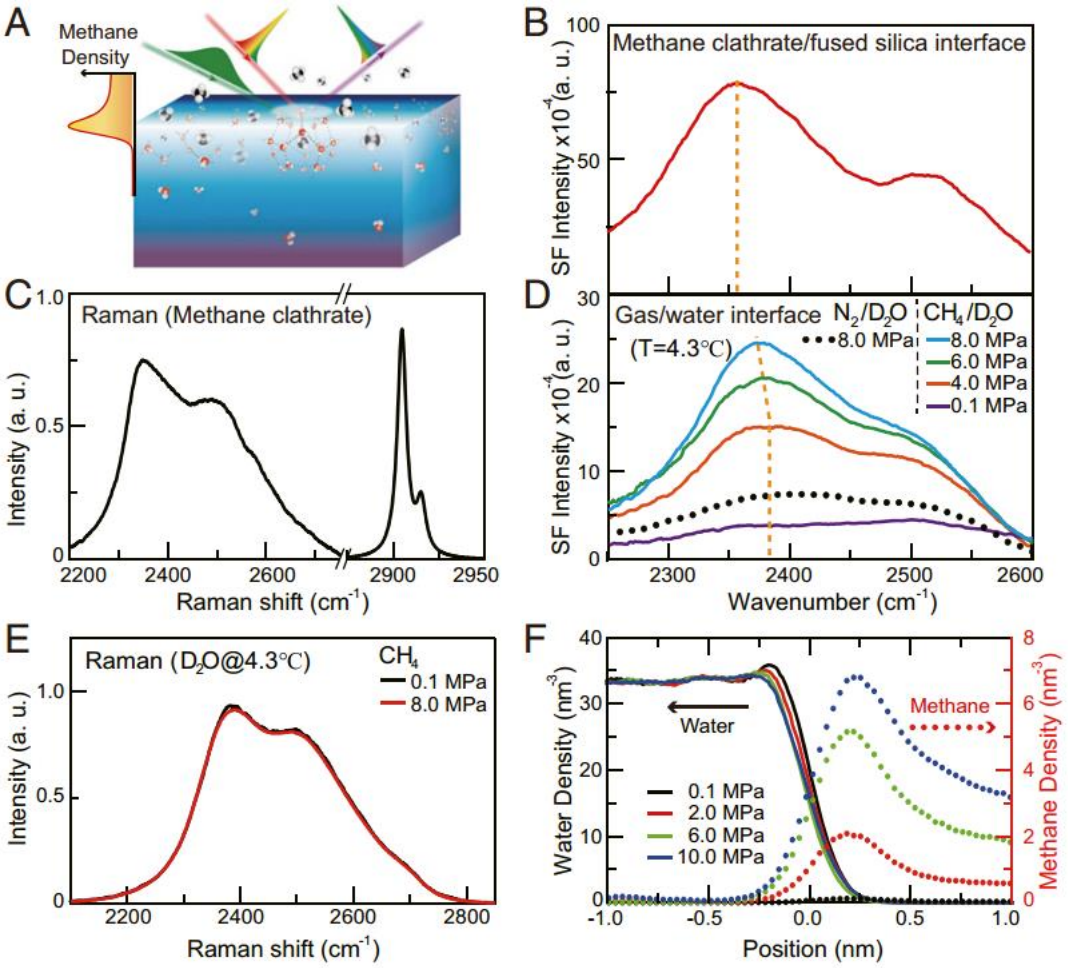
https://www.sciencedirect.com/science/article/pii/S0378381219300469

➡ **Sample Preparation for Experiment at Gas–Water Interface:** Ultrapure deionized H_2O or deuterated water was held in a fused silica cell placed inside the high pressure chamber.



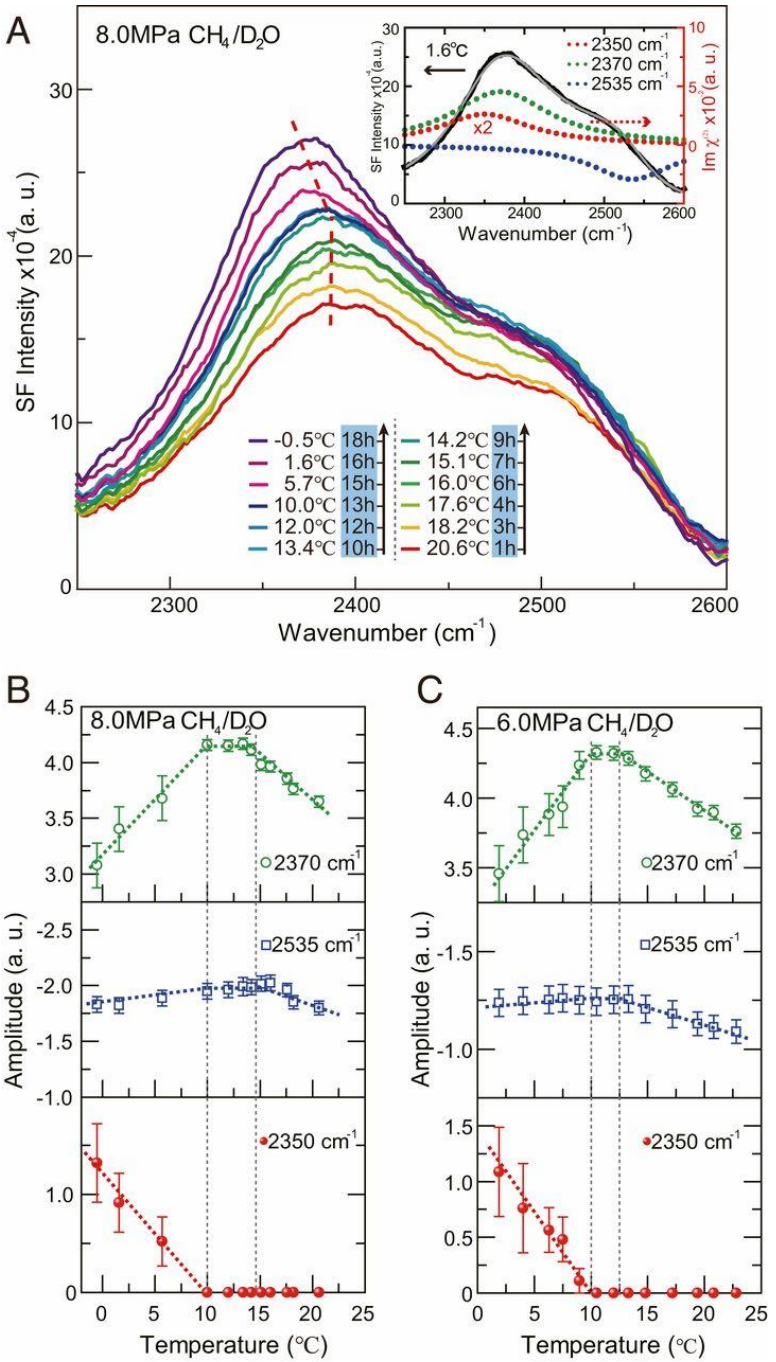
Results

Spectral characterization of solid methane clathrate and the high-pressure methane–water interface



(*A*) Schematic of SFVS arrangement for probing the methane–water interface. (*Inset*, *Left*) Density profile of methane in the interfacial region. (*B*) SF spectrum of polycrystalline methane–D_2O clathrate grown on fused silica. (*C*) Raman spectrum of the same sample as in *B*, showing characteristic feature of the s-I crystalline clathrate. (*D*) SF spectra of methane–water (D_2O) interface at 4.3 °C with different methane pressures from 0.1 to 8.0 MPa. SF spectrum of 8.0 MPa nitrogen–D_2O interface (dotted curve) is also presented for comparison. (*E*) Raman spectra of bulk water (D_2O) at 4.3 °C under methane pressures of 0.1 and 8.0 MPa. (*F*) Calculated molecular density profiles of water and methane in the interfacial region versus pressure by MD simulations.

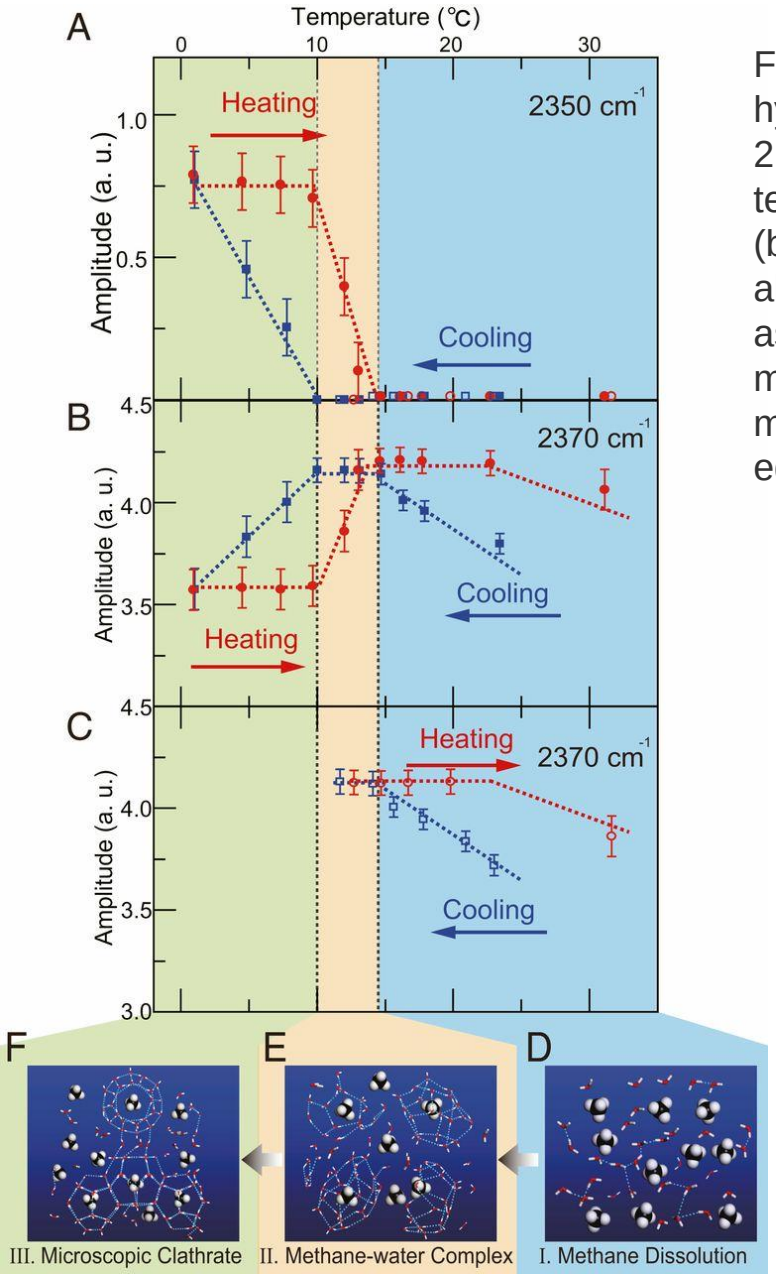
Nucleation of methane clathrate at the gas–water interface



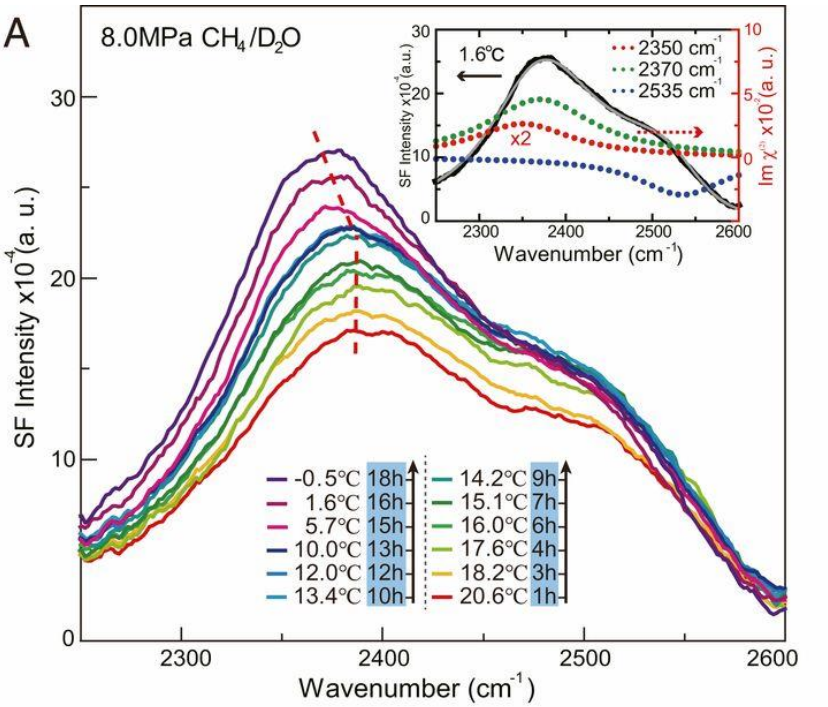
Temperature dependence of SF spectra at the methane–D_2O interface. (*A*) A set of SF spectra in the OD stretching region for the methane–water interface under 8.0 MPa of methane with temperature decreasing from 20.6 °C down to −0.5 °C. Times at which spectra at different temperatures were taken after start of cooling are indicated. (*Inset*) Representative theoretical fit (gray) of the SF spectrum (black) at 1.6 °C and the imaginary components (dotted curves) of the 3 modes composing the spectra. The amplitudes of the 3 modes as functions of temperature deduced from fitting of the SF intensity spectra are presented in *B* for 8.0 MPa and *C* for 6.0 MPa of methane vapor pressure. The black dashed vertical lines mark the temperature ranges of 3 different stages of structural changes at the methane–water interface. The colored dashed lines serve as a guide to the eye. The phase equilibrium temperatures under 8.0 and 6.0 MPa are ∼14.0 and ∼11.5 °C, respectively.

T (°C)	A_1 (2350 cm^{-1})	A_2 (2370 cm^{-1})	A_3 (2535 cm^{-1})
20.6	0.0	3.65	-1.80
18.2	0.0	3.76	-1.85
17.6	0.0	3.86	-1.96
16.0	0.0	3.96	-2.02
15.1	0.0	3.98	-2.02
14.2	0.0	4.11	-1.99
13.4	0.0	4.17	-1.99
12.0	0.0	4.15	-1.96
10.0	0.0	4.16	-1.95
5.7	0.5	3.68	-1.89
1.6	0.9	3.40	-1.82
-0.5	1.3	3.08	-1.83

Structural Hysteresis at the Methane–Water Interface during Cooling–Heating Cycle



Formation/disintegration of methane clathrate showing structural hysteresis during cooling–heating cycles. Amplitude of (*A*) the 2,350 cm^{-1} mode and (*B*) the 2,370 cm^{-1} mode versus temperature of the methane–water interface that was first cooled (blue color) down to 0 °C and then heated up to 31 °C (red color), all under fixed methane vapor pressure of 8.0 MPa. (*C*) Same as *B*, but with temperature first cooled down to 12 °C. Formation of methane clathrate appears to go through the successive stages of molecular arrangement, I to III, sketched in *D*–*F*. The phase equilibrium temperature under 8.0 MPa is ~14.0 °C



Summary

➡ Surface-specific SFVS have used to study nucleation and dissociation of methane clathrate.

➡ This study confirmed that with water under high-pressure methane vapor, nucleation and growth of methane clathrate starts at the methane–water interface.

➡ Methane–water interfacial structure undergoes 3 stages of changes-

- In the first stage with a fixed high-vapor pressure, the solvated methane concentration increases with decrease of temperature.
- In the second stage, a cage-like structure of water with an embedded methane molecule seems to appear in dynamical equilibrium with water and serve as nuclei or seeds for later possible growth of methane clathrate, while the host water structure remains nearly unchanged.
- In the third stage, some of the nuclei in the interfacial layer reach the critical size and grow into methane clathrate.