Supporting Information

Experimental methods

Methane hydrate was formed by pressurizing a glass bulb containing freshly powdered ice with 100% ^{13}C enriched methane gas at about 4.8 MPa at 271-274 K for about two weeks. Excess methane gas was vacuum pumped from the glass bulb and the resulting methane hydrate in the glass bulb was sealed with a torch while cooling the sample with liquid nitrogen; sufficient hydrate melted to yield the equilibrium pressure of 1.4 MPa (Reference 11) while the sealed sample was stored in a freezer at 253 K until use. A fresh methane + water sample was prepared by condensing a quantity of 100% ^{13}C enriched methane gas, sufficient to yield a final pressure of about 1 MPa, into a glass bulb containing water and sealing the bulb with a torch while cooling the sample with liquid nitrogen; the sample was stored at room temperature until use.

NMR spectra were recorded on a Chemagnetics CMX Infinity 400 NMR spectrometer operating at 100.6 MHz for ^{13}C using a ^{1}H decoupling field of 50 kHz unless indicated otherwise. The external chemical shift reference was the methyl carbon resonance of hexamethylbenzene, which was assigned a chemical shift of 17.36 ppm. Magic-angle spinning (MAS) was accomplished by placing the sealed glass bulb in a Chemagnetics 7.5 mm Pencil rotor.

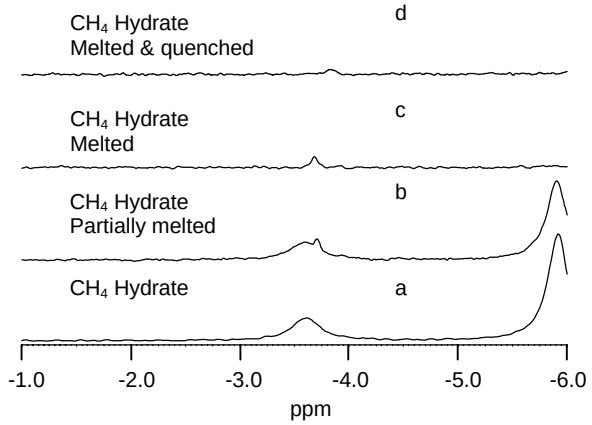

Figure 1S. 100.6 MHz ^{13}C MAS NMR spectra of 100% ^{13}C enriched CH_4 hydrate in various states of decomposition. Same spectra as shown in Figure 1 but on scale expanded about the CH_4 hydrate dodecahedral cage. a) CH_4 hydrate at 243 K and 1.4 MPa, b) partially melted CH_4 hydrate at 273 K and 2.6 MPa, c) completely melted CH_4 hydrate at 275 K and 3.1 MPa, and d) completely melted and quenched CH_4 hydrate at 253 K and 2.9 MPa.

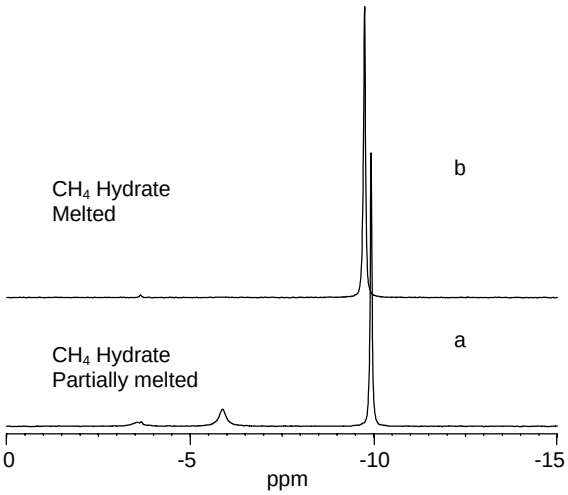

Figure 2S. 100.6 MHz ^{13}C MAS NMR spectra of 100% ^{13}C enriched CH_4 hydrate in various states of decomposition. Spectra are those shown in Figures 1b and 1c but drawn on a scale to illustrate that the methane gas phase peak intensity dominates the spectrum.