

**Cage occupancy of methane clathrate hydrates in the ternary H<sub>2</sub>O-NH<sub>3</sub>-CH<sub>4</sub> system.**

Supporting Information

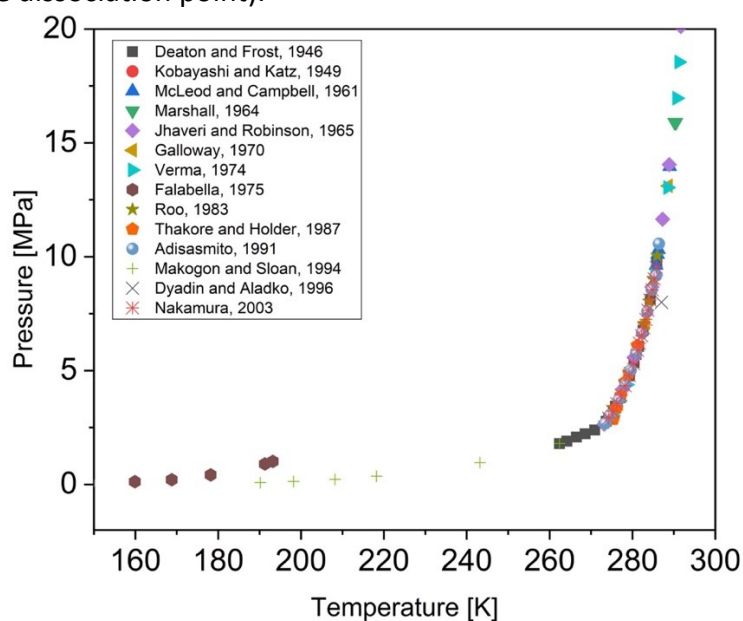
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## EXPERIMENTAL METHODS.

**Sample Preparation.** Samples were prepared using a stock H<sub>2</sub>O-NH<sub>3</sub> solution (~ 28-30 wt%) diluted with water (HPLC grade, Fisher Scientific, Certified) to achieve concentration within the range 0-22 wt%. The solution was first inserted inside the sample cell to be cooled down at 273 K ( $\pm$  0.1 K) with a modified temperature controlled stage (Linkam Scientific Instruments Ltd., UK) including a home-made high-pressure optical cell equipped with a 2 mm thick sapphire optical window. Methane pressure (50 bar, 100 bar and 200 bar) was then added during 1 or 2 minutes with a homemade set up including a PM High Pressure pump (Top Industrie, Vaux-le-Penil, France) which can contain 100 cm<sup>3</sup> of gas up to 500 bars. The temperature was cooled down until 170 K (around 1 h), where methane clathrate is stable at atmospheric pressure (Fig. S1), and after an equilibration time of 20-30 minutes, the sample was depressurized (slow depressurization, around 1-2 minutes) to minimize the CH<sub>4</sub> gas peak intensity in Raman spectra (which allow to study LC and SC occupancies). An additional equilibration time of around 20 min was then allowed before acquiring Raman spectroscopy data. Once cage occupancies data were collected (after around 1-2 h), the sample was re-pressurized with the same pressure, the temperature is then slowly increased to obtain the dissociation temperature of CH<sub>4</sub> clathrate (heating rate of 5 K/min at the beginning and 1 K/min close to the dissociation point).

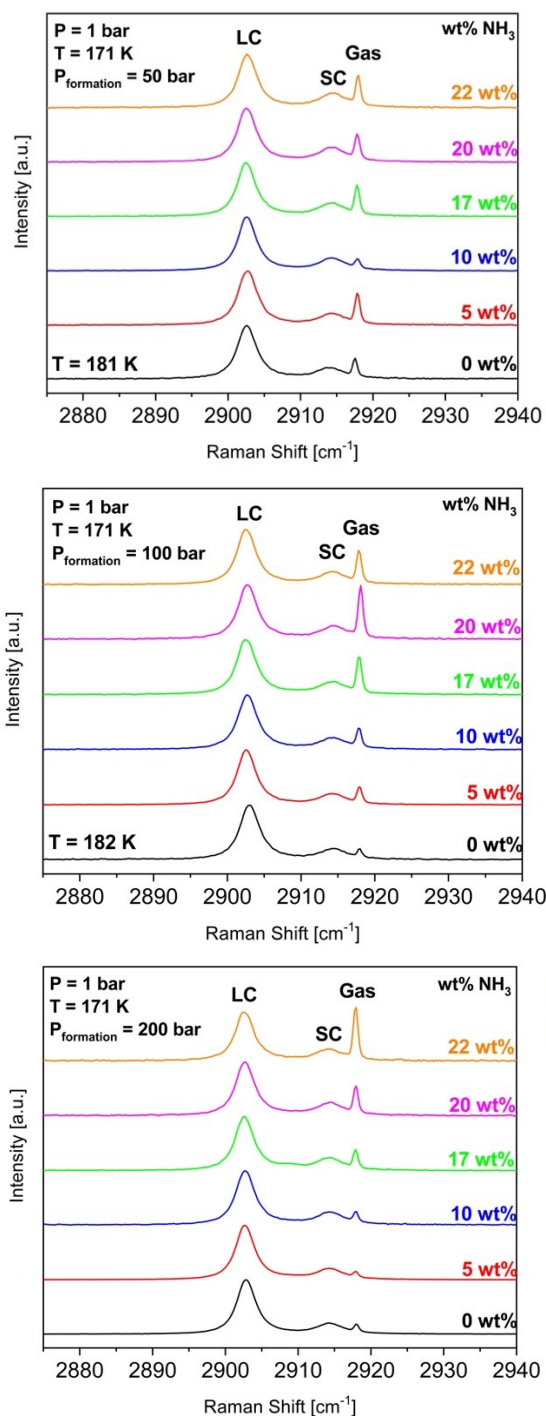


**Fig. S1:** Phase diagram of pure CH<sub>4</sub> clathrate hydrate (adapted from Sloan).

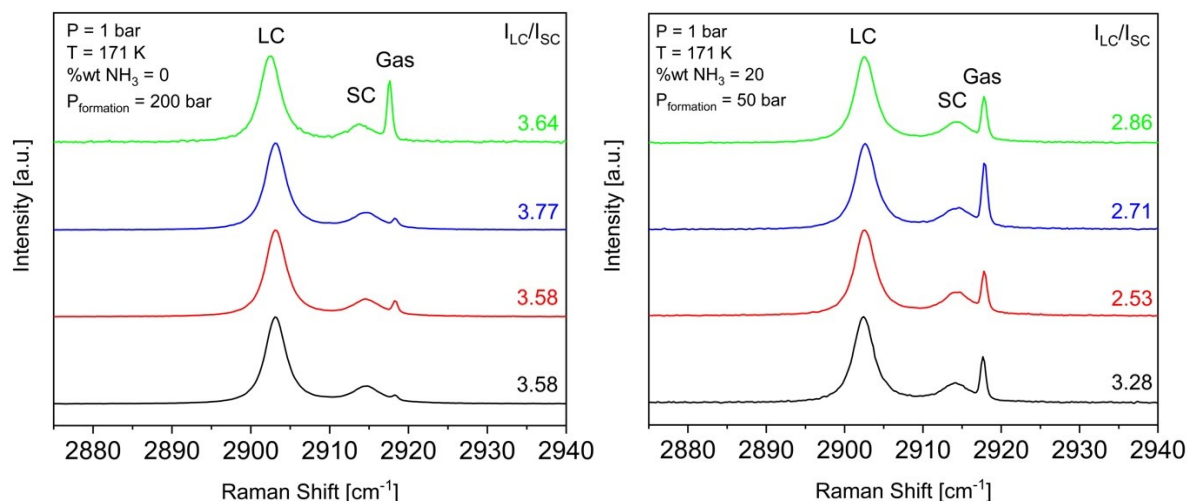
**Raman spectroscopy.** Raman spectra were recorded with a Labram microspectrometer (Horiba Jobin Yvon, Villeneuve d'Ascq, France) using a 514 nm wavelength laser as excitation source. A 50X objective allowed for focusing of the incident laser beam and collection of the Raman scattering. The Raman scattering was dispersed by a holographic grating of 2400 lines/mm (high resolution) and analyzed by a Peltier-cooled CCD detector (Andor, Belfast, UK). Thus, the intensity of different regions of the spectrum can be measured with a spectral resolution of 0.8 cm<sup>-1</sup> (pixel resolution of 0.2 cm<sup>-1</sup>). The calibration of the spectrometer was done using the 520.7 cm<sup>-1</sup> mode of a silicon sample. Due to the very high resolution, Raman data were collected in a range of 2800 to 3800 cm<sup>-1</sup> with an acquisition time of 50s x 10 (or 4), and in four different spots in the sample to average the cage occupancy results. Cage

occupancy data have been recorded in four different places in the sample to calculate an average and having a more accurate and representative result. The error bars in Fig. 2 represent the standard deviation of these average. Spectra are fitted with OriginLab and LabSpec using pseudoVoigt functions (mixture of a Lorentzian and a Gaussian function).

## RESULTS



**Fig. S2** : Raman signatures of CH<sub>4</sub> in the gas phase and in the clathrate phase (LC and SC occupancies) at different NH<sub>3</sub> concentrations (0-22 wt%) and formation pressures (50 bar, 100 bar and 200 bar).



**Fig. S3:** Raman signatures of  $\text{CH}_4$  in the gas phase and in the clathrate phase (LC and SC occupancies) of samples formed with an ammonia concentration of 0 wt% (left) and 20 wt% (right) and at 200 bar and 50 bar, respectively. The four spectra represent the four different spots (the first being at the bottom in black line and the fourth at the top in green line) in the sample where data were collected to calculate the  $I_{\text{LC}}/I_{\text{SC}}$  average ratio of Fig. 2.

wt% $\text{NH}_3$	$T_{\text{disso}}$ (50 bar) [K]	$T_{\text{disso}}$ (100 bar) [K]	$T_{\text{disso}}$ (200 bar) [K]
0	280.4	286.1	292.4
5	278.6	283.8	287.4
10	268.8	275.3	282.8
17	254.0	261.5	270.2
20	244.2	252.7	260.0
22	235.9	247.4	252.8

**Table S1:** Dissociation temperatures of  $\text{CH}_4$  clathrates depending on  $\text{NH}_3$  concentration and formation pressure.

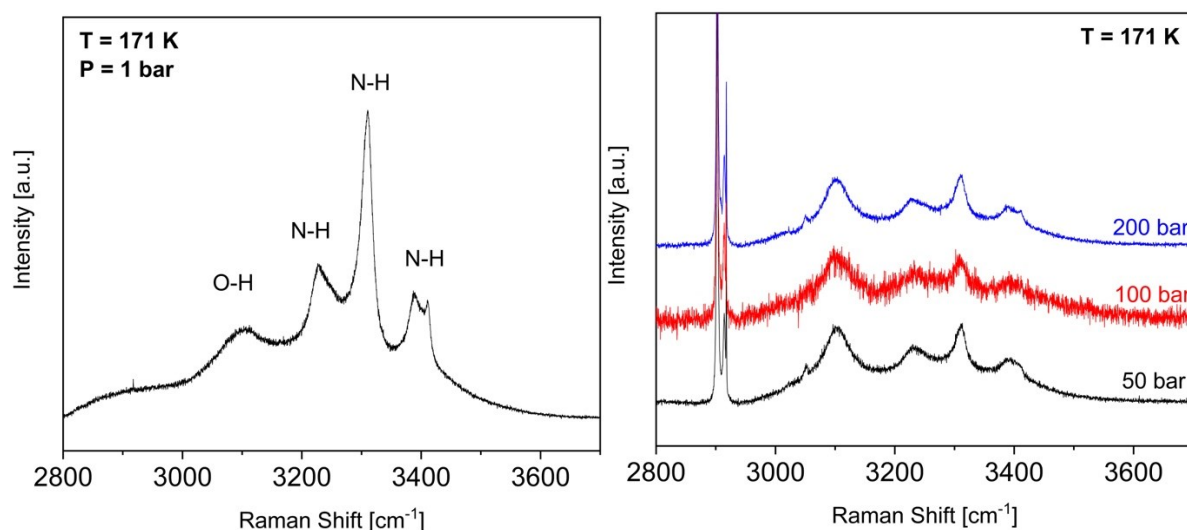
$P_{\text{formation}}$	50 bar	100 bar	200 bar
$\nu_{1,\text{LC}}$ [ $\text{cm}^{-1}$ ]	2902.7	2902.6	2902.7
$\nu_{1\text{SC}}$ [ $\text{cm}^{-1}$ ]	2914.4	29014.3	2914.4
$\nu_{1,\text{Gas}}$ [ $\text{cm}^{-1}$ ]	2917.8	2917.8	2917.8

**Table S2:** Raman signatures of gaseous and enclathrated  $\text{CH}_4$  at various formation pressures.

NH <sub>3</sub>	0 wt%		5 wt%		10 wt%		17 wt%		20 wt%		22 wt%	
<b>50 bar</b>	3.67	<i>0.13</i>	3.40	<i>0.28</i>	3.03	<i>0.09</i>	2.83	<i>0.13</i>	2.86	<i>0.32</i>	2.78	<i>0.21</i>
<b>100 bar</b>	3.86	<i>0.22</i>	3.71	<i>0.08</i>	3.30	<i>0.22</i>	3.14	<i>0.24</i>	2.93	<i>0.10</i>	3.05	<i>0.14</i>
<b>200 bar</b>	3.64	<i>0.09</i>	3.63	<i>0.20</i>	3.12	<i>0.29</i>	3.33	<i>0.23</i>	3.01	<i>0.10</i>	3.10	<i>0.23</i>

**Table S3:**  $I_{LC}/I_{SC}$  intensity ratio average (grey column) of methane clathrate formed in an ammonia solution depending on ammonia concentration at 50 bar, 100 bar and 200 bar. Standard deviation (italic white column) of these averages represents the errors bars in Fig. 3.

Fig. S4 shows the high wavenumber region (2900-3600  $\text{cm}^{-1}$ ) of the samples formed in a  $\text{H}_2\text{O-NH}_3$  solution consisting of 20 wt%  $\text{NH}_3$ . As in the Fig. 4, a shoulder is observed around 3400  $\text{cm}^{-1}$ . However, in this case, the shoulder is even more pronounced in the  $\text{H}_2\text{O-NH}_3$  solution. This means that the presence of this peak is not related to the formation of methane clathrate within an ammonia solution. Thereby, the vibrational mode at 3400  $\text{cm}^{-1}$  can not be the expression of the  $\text{NH}_3$  incorporation in the clathrate cages. Moreover, Ujike et al. found this peak in  $\text{H}_2\text{O-NH}_3$  solution at 200 K using polarized Raman spectroscopy.



**Fig. S4** *Left:* O-H and N-H stretching modes of  $\text{H}_2\text{O-NH}_3$  solution concentrated at 20 wt%. *Right:* O-H and N-H stretching modes of  $\text{CH}_4$  clathrate formed within a 20 wt%  $\text{NH}_3$  solution at 50 bar, 100 bar and 200 bar.

## REFERENCES

- E. D. Sloan, C. A. Koh, *Clathrate Hydrates of Natural Gases*; CRC Press: Boca Raton, FL, **2008**.
- T. Ujike, Y. Tominaga, Raman Spectral Analysis of Liquid Ammonia and Aqueous Solution of Ammonia. *J. Raman Spectrosc.* **2002**, *33*, 485-493.