

Supplementary materials for: “In-situ abiogenic methane synthesis from diamond and graphite under geologically relevant conditions”

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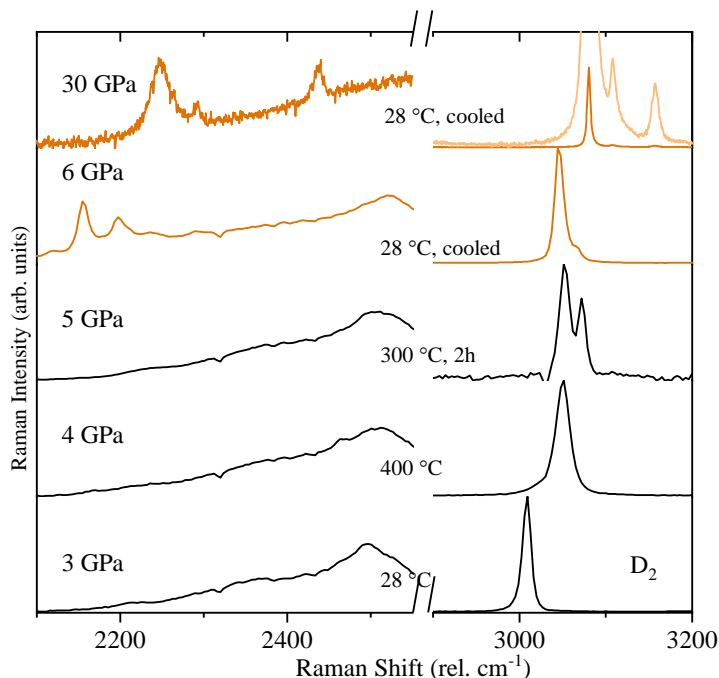
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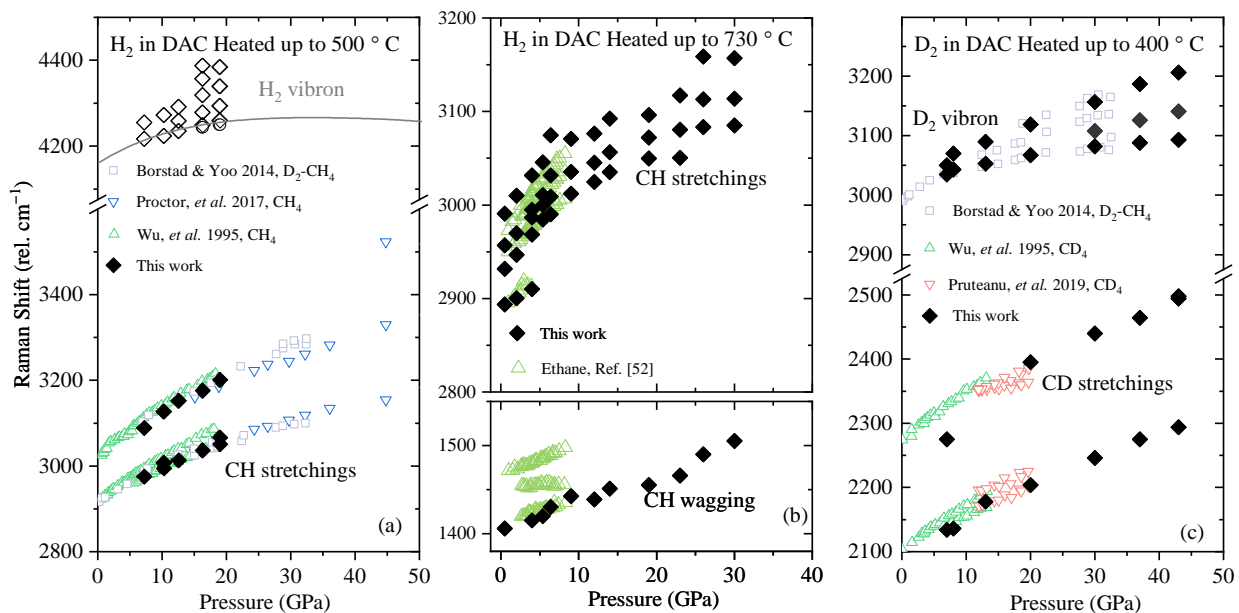
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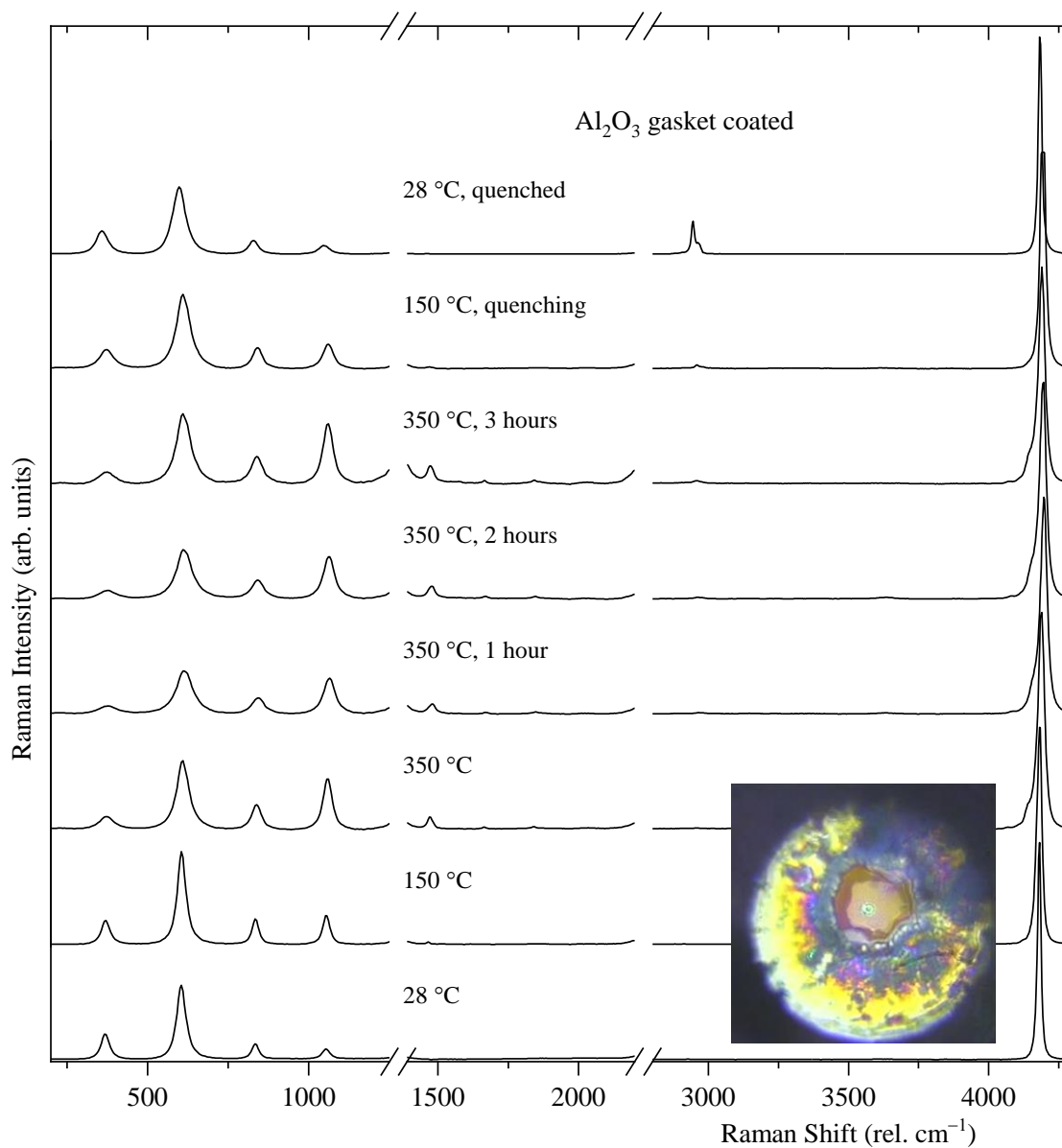


Supplementary Figure 1. Resistive heating of deuterium in diamond anvil cell. During the heating cycle pressure was increasing from 3 to 6 GPa. After quenching pressure was increased to 30 GPa at room temperature to compare the frequencies of the synthesised product with those of deuterated methane (see Supplementary Figure S2).

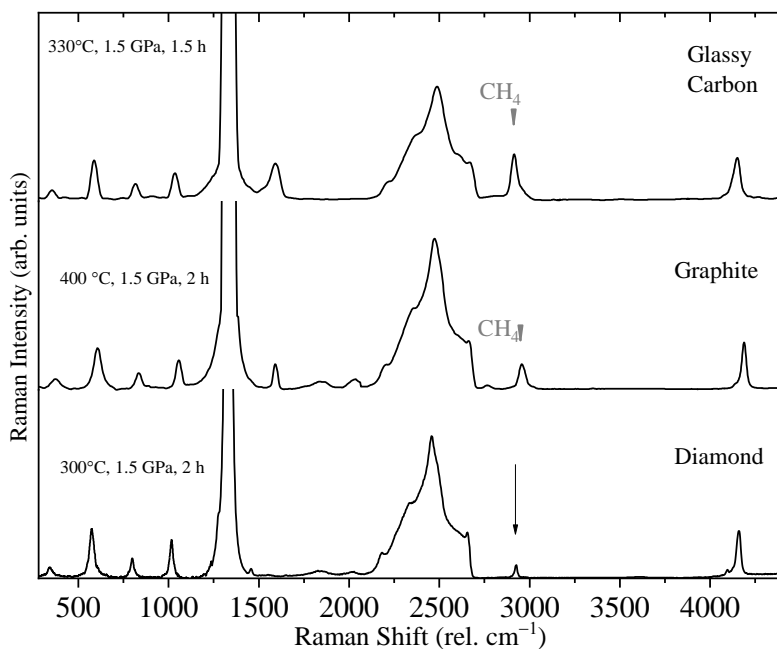


Supplementary Figure 2. Comparison of the Raman frequencies of the synthesised products in our experiments during compression with data from literature. (a) Methane and hydrogen. (b) Ethane. (c)

Deuterated methane. The literature data for comparison are taken from: Wu, *et al* [1] and Pruteanu, *et al.* [2] for CD₄; Borstad, *et al.* [3] and Proctor *et al.* [4] for D₂ and CH₄; Howie, *et al.* [5] for H₂.



Supplementary Figure 3. Raman spectra of H₂ during a heating cycle at 3 GPa using a coated gasket with an insulating Al₂O₃ layer. In this experiment the rhenium gasket was coated with Al₂O₃ chemically vapour deposited 500 nm thick on both sides.



Supplementary Figure 4. Comparison of resistive heating of hydrogen in DAC. From bottom to top: H₂ in the chamber, hydrogen with graphite and glassy carbon with hydrogen.

Supplementary Table 1. Summary of the experimental runs

N:	gas ket	Lining to protect gasket	max T °C	Time of heating run, approx.	Pressure during experiment	Product
H ₂	Re	Au	705 °C	Kept for 10 min 705 °C	2-4 GPa	CH ₄
H ₂	Re	Au	605 °C	Kept for 1 hour 605 °C	2-4 GPa	CH ₄
H ₂	W	Au	375 °C	Kept for 20 min 375 °C	2-4 GPa	CH ₄
H ₂	Re	Au	550 °C	Kept for 2 hours at 550 °C	1-3 GPa	CH ₄
H ₂	W	None	600 °C	Kept for 10 min 600 °C	1-3 GPa	CH ₄
H ₂	Re	None	730 °C	Kept for 2 hours at 500 °C	1-3 GPa	C ₂ H ₈ (ethane)
H ₂	W	None	550 °C	Kept for 2 hours at 400 °C	1-3 GPa	CH ₄
H ₂	W	None	550 °C	Kept for 2 hours at 400 °C	1-3 GPa	CH ₄
H ₂	Re	None	550 °C	Kept for 2 hours at 400 °C	0.5-1.8 GPa	CH ₄
H ₂	Re	None	400 °C	Kept for 3 hours at 400 °C	1-3 GPa	CH ₄
H ₂	Re	None	400 °C	Kept for 3 hours at 400 °C	1-3 GPa	CH ₄
H ₂	Re	None	330 °C	Kept for 3 hours at 330 °C	1-2 GPa	CH ₄
H ₂	Re	Diamonds coated with Al ₂ O ₃ and gasket coated with Al ₂ O ₃	500 °C	Kept for 3 hours at 360 °C	3-4 GPa	Traces of methane after the coating peeled off
H ₂	Re	Gasket coated with Al ₂ O ₃	350 °C	Kept for 3 hours at 350 °C	1-4 GPa	CH ₄

H ₂	Re	Diamonds coated with Al ₂ O ₃	500 °C	Kept for 3 hours at 350 °C	2-4 GPa	Traces of methane after the coating peeled off
D ₂	Re	None	750 °C	Kept for 1 hour at 325 C. T was increased to 750 °C	2-4 GPa	CD ₄
D ₂	Re	Au	500 °C	Kept for 1 hour at 300 C	2-4 GPa	CD ₄
D ₂	Re	Au	480 °C	Kept for 2 hours at 480 C	2-4 GPa	CD ₄
D ₂	W	none	750 °C	Kept for 1 hour at 300 C	2-4 GPa	CD ₄

[1] Wu, Y., Sasaki, S. & Shimizu, H. High-pressure Raman study of dense methane: CH₄ and CD₄. *Journal of Raman Spectroscopy* 26, 963–967 (1995).

[2] Pruteanu, C. G. The effect of deuteration on the optical spectra of compressed methane. *AIP Advances* 9, 045033 (2019).

[3] Borstad, G. M. & Yoo, C.-S. Hydrogen bonding induced proton exchange reactions in dense D₂-NH₃ and D₂-CH₄ mixtures. *The Journal of Chemical Physics* 140, 044510 (2014).

[4] Proctor, J. E., Maynard Casely, H. E., Hakeem, M. A. & Cantiah, D. Raman spectroscopy of methane (CH₄) to 165 GPa: Effect of structural changes on Raman spectra. *Journal of Raman Spectroscopy* 48, 1777 – 1782 (2017).

[5] Howie, R. T., Guillaume, C. L., Scheler, T., Goncharov, A. F., Gregoryanz, E. Mixed molecular and atomic phase of dense hydrogen. *Physical Review Letters* 108, 125501 (2012).