ESRF	**Experiment title:** X-ray diffraction study of Methane up to 450 GPa in a toroidal-DAC and observation of its dissociation into diamond	**Experiment number**: HC4449
Beamline: ID15b	**Date of experiment**: from: 13/04/2021 to: 17/04/2021	**Date of report**: 13/09/2021
Shifts: 12	**Local contact(s)**: Gaston Garbarino, Michael Hanfland	*Received at ESRF:*

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Report:
Scientific background and objectives

The characterization of the physico-chemical properties of the C-H system under high-pressure and high temperature is of great importance in many fields such as organic, bio and petroleum chemistry as well as in planetary science. As the simplest and most fundamental hydrocarbon, Methane (CH_4) has been extensively studied by first principle calculations predicting the stability of various CHx compounds in the 0-300 GPa range and their disproportionation reactions. However X-ray diffraction experiments reached only 200 with questionable data quality [1], in which a phase transition at around 75 GPa was allegedly observed. In more recent Raman spectroscopy experiments [2], other transition events seem to happen around 45 GPa and 110 GPa. The goal of our experiment was to obtain better X-ray diffraction data on CH_4 in order to update the methane equation of state and to elucidate in particular whether or not it undergoes any phase transitions, as well as test the stability of CH_4 at high pressure and high temperateure. According to theoretical studies, at pressures higher than 300 GPa and ambient temperature, diamond should be the most stable phase and so the dissociation of CH_4 to diamond and dihydrogen could be observed. Combining X-ray diffraction with laser heating would give additionnal information on CH_4 dissociation at high temperature, but laser heating was not available on ID15B.

Experimental details and results

Since it was not possible to laser heat sample on site we focussed our efforts on the methane EOS and structural properties. Four diamond anvil cells were prepared with various sample configurations. A first cell mounted with diamonds with culets of 150µm was loaded with pure CH_4 and a single crystal was carefully grown at 1 GPa. GPa. Measurement were performed up to 120 GPa, leading to an updated compression curve for CH_4 (see fig. 1). Notably, we did not observe any phase transition from 20 GPa to 120 GPa, invalidating the previously reported transitions. A second cell was prepared with diamonds with a 33µm culet size and loaded with pure CH_4. In this cell, the sample size (12µm in diameter) was too small for the X-ray beam (3-4µm in diameter) and the CH_4 diffraction signal was complely hidden by the diffraction of the Au gauge and the Rh gasket. Further experiments with this sample geometry dedicated to reach 300 GPa will require a ~1 micron beam diameter.

Two other cells were loaded with a CH_4-He fluid mixture. After loading, the pressure was increased to reach the demixtion point between pure solid methane and pure fluid helium. A single crystal of CH_4 was then selected and slowly grown surrounded by helium (see fig. 2).
The first cell used diamonds with a culet size of 400µm and measurement were performed up to 25 GPa. Using the resulting high data quality (see fig. 3), we retrieved the full lattice structure of CH_4 (see fig. 4) and thus confirmed the latest proposed structure [3] that was in disagreement with all previous works. With the second cell and its culet size of 150µm, we hoped to reach more than 100 GPa and to compare the results with the pure CH_4 run, but the diamond anvils broke due to helium diffusion in the diamond.

In the present experiment, we accurately measured the EOS of methane up to 120 GPa. We also obtained complete structural data by measuring the diffraction of a single crystal of methane in helium. We now need to extend these measurements to the multi-megabar range. This can be done with the same sample geometry, using a sub-micron X-ray beam. A new proposal will be submitted to pursue this study.

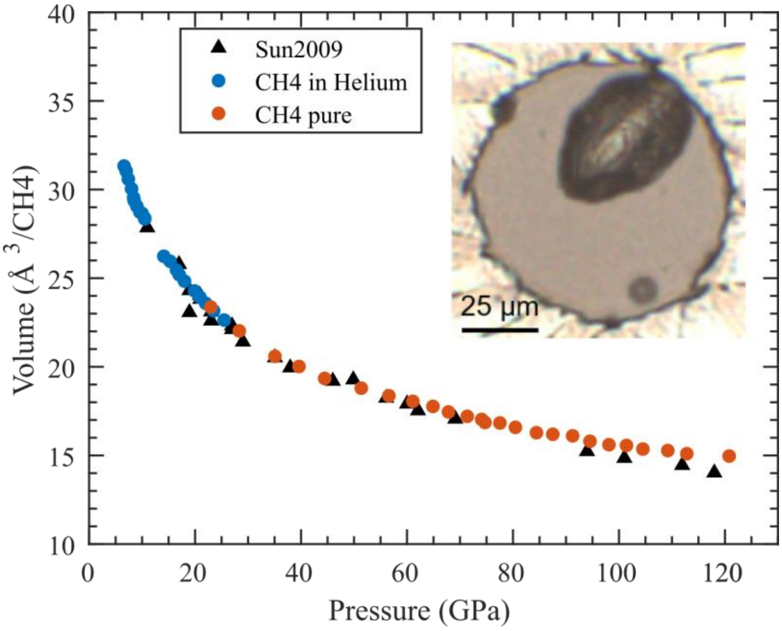

Figure 1: Compression curve of CH_4 and CH_4 in helium. Inset: single crystal of CH_4 in helium

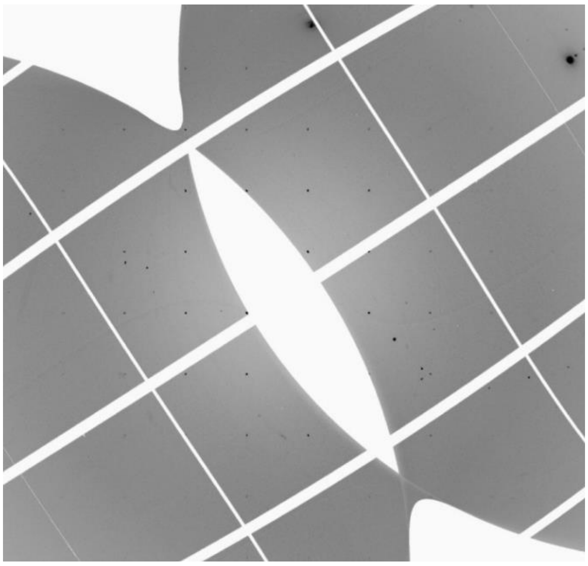

Figure 3: Unwarp (h -1 l) image, CH_4 in helium at 14 GPa

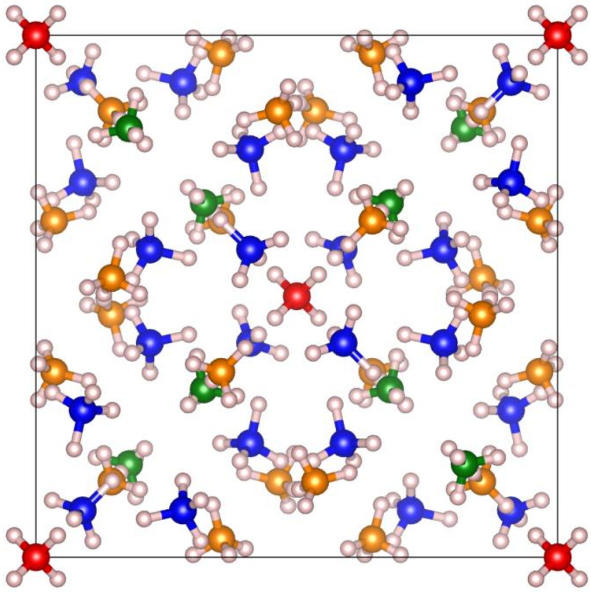

Figure 4: Full I-43m structure of CH_4 at 14 GPa

[1] L. Sun *et al.*, *Chemical Physics Letters* **473**, 72-74 (2009).
[2] J.E. Proctor *et al.*, *Journal of Raman Spectroscpy* **48** 1777-1782 (2017).
[3] Maynard-Casely *et al.*, *The Journal of Chemical Physics* **141**, 23 (2014).