

High Pressure Hydrocarbons Revisited: From Van Der Waals Compounds to Diamond

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Abstract

Methane and other hydrocarbons are major components of the mantle regions of icy planets. Several recent computational studies have investigated the high-pressure behaviour of specific hydrocarbons [1-5]. To develop a global picture of hydrocarbon stability, to identify relevant decomposition reactions, and probe eventual formation of diamond, a complete study of all hydrocarbons is needed. Using density functional theory calculations we survey here all known C-H crystal structures augmented by targeted crystal structure searches to build hydrocarbon phase diagrams in the ground state and at elevated temperatures. We find that an updated pressure-temperature phase diagram for methane is dominated at intermediate pressures by $\text{CH}_4\text{:H}_2$ van der Waals inclusion compounds. We then discuss the decomposition processes in carbon rich samples.

1. Introduction

Methane has a complex phase diagram [1] which is crucial for describing the convection processes within planetary interiors. It has long been suggested that methane will undergo decomposition into diamond and hydrogen at temperatures and pressures found in icy planets. If methane were to decompose to form diamond, the latter would precipitate whereas any remaining hydrocarbons might dissipate into the atmosphere, potentially providing a missing hydrocarbon production mechanism in atmospheric models [6]. This computational study aims to build a more complete picture of hydrocarbons under high pressure ranging from the hydrogen rich $\text{CH}_4\text{:H}_2$ inclusion compounds to diamond formation in carbon rich compounds which have been the subject of recent shock experiments [7].

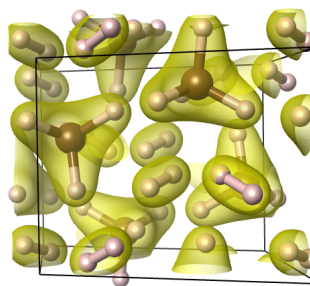


Figure 1: Crystal structure and charge density of $\text{CH}_4(\text{H}_2)_2$ at 200 GPa.

2 Methods

We performed electronic structure calculations on all hitherto proposed C-H structures including geometry optimisations, and phonon calculations [8]. Zero point energy and entropy calculations were used to estimate the Gibbs free energy within the harmonic approximation to estimate phase stability at finite temperatures. To augment the pre-existing structures, we performed structure searches for various hydrogen-rich hydrocarbons. Unbiased particle swarm optimisation searches were carried out using the CALYPSO code [10] interfaced with CASTEP [9] on a range of C_xH_{1-x} stoichiometries ($x \leq 0.25$).

3 Results

The updated phase diagram for methane is shown in figure 2. We find that it is dominated by a series of van der Waals inclusion compounds between 70 and 150 GPa. Our structure searches reveal at least four such compounds, with $\text{CH}_4\text{:H}_2$ stoichiometries of 2:1, 1:1, 2:3, and 1:2, are competitive in this pressure range and have common methane host networks. The 1:2

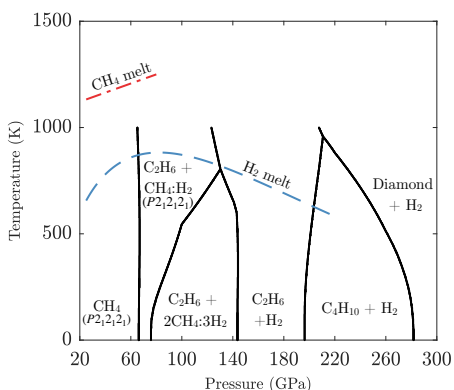


Figure 2: Pressure - Temperature phase diagram for CH_4 calculated using the harmonic approximation.

compound (figure 1) contains 20 *wt* - % releasable hydrogen, on par with the best known hydrogen storage materials.

In addition to the calculations for CH_4 , we present the composition-pressure phase diagram for hydrocarbons in figure 3. It can be seen that CH_2 remains metastable over a large pressure range, preventing diamond formation until close to 300 GPa. This has implications in the interpretation of recent shock experiments on polyethylene [7].

4. Summary and Conclusions

In conclusion, we present an internally consistent computational study of a wide range of hydrocarbon compounds, and discuss their stability as function of pressure, temperature, and composition, based on semi-local density functional theory calculations and the harmonic approximation.

We also present phase diagrams for more carbon-rich phases, CH_2 and CH , which have been studied in recent dynamic compression experiments. These phase diagrams disagree with experimental findings regarding diamond formation (similar to methane), but we explore possible explanations around the metastability of the hydrocarbon phases and the lack of enthalpic gains unless full decomposition into diamond and hydrogen is favourable.

The interiors of icy planets are chemically very diverse, nonetheless, this study presents a step forward in our understanding of hydrocarbon diversity and their evolution with pressure, and enables follow-up studies to focus on relevant hydrogen-carbon mixtures.

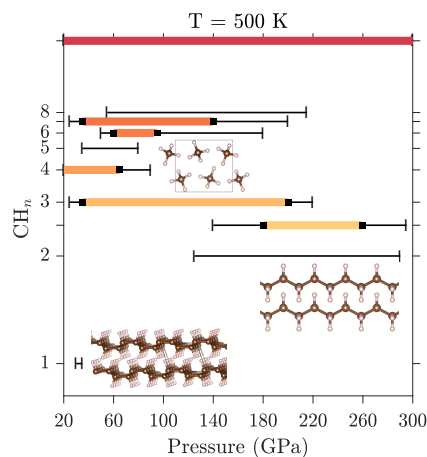


Figure 3: Pressure - composition phase diagram for C-H compounds calculated using the harmonic approximation. Thin lines represent metastability regions.

Acknowledgements

This work was supported by studentship funding from EPSRC under grant no. EP/L015110/1. Computing resources provided by the UK national high performance computing service, ARCHER, and the UK Materials and Molecular Modelling Hub, which is partially funded by EPSRC (EP/P020194), and for which access was obtained via the UKCP consortium funded by EPSRC grant no. EP/P022561/1, are gratefully acknowledged.

References

- [1] G. Gao *et al.* *J. Chem. Phys.* **2010**, *133*, 144508.
- [2] G. Saleh and A.R. Oganov *Sci. Rep.* **2016**, *6*, 1–9.
- [3] X.D. Wen *et al.* *Proc. Natl. Acad. Sci.* **2011**, *108*, 6833–6837.
- [4] H. Liu, I.I. Naumov, and R.J. Hemley. *J. Phys. Chem. Lett.* **2016**, *7*, 4218–4222.
- [5] Liu, Y *et al.*. *RSC Adv.* **2014**, *4*, 37569–37574.
- [6] B. Bézarard *et al.* *J. Geophys. Res.* **1991**, *96*, 18961.
- [7] N. J. Hartley *et al.* *Sci. Rep.* **2019**, *9*, 4196.
- [8] L. J. Conway and A. Hermann *Geosciences*. **2019**, accepted.
- [9] S. J. Clark, *et al.* *Z. Krist.* **2005**, *220*, 567–570.
- [10] Y. Wang *et al.* *Comput. Phys. Commun.* **2012**, *183*, 2063–2070.