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This is the submitted version of a paper published in *Minerals*.

Citation for the original published paper (version of record):

Kudryavtsev, D., Kutcherov, V., Dubrovinsky, L., Serovaiskii, A. (2020)  
High-pressure chemistry of propane  
*Minerals*

Access to the published version may require subscription.

N.B. When citing this work, cite the original published paper.

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<http://urn.kb.se/resolve?urn=urn:nbn:se:kth:diva-267050>

## Abstract

This study is a comprehensive research of the propane's high-pressure and high-pressure high temperature behaviour using diamond-anvill cell technique combined with vibrational spectroscopy. As we have found, propane while being exposed to the high pressures (5-40 GPa) could exhibit three solid-solid phase transitions. With the applying of laser heating technique, propane could react with the formation of various hydrocarbon compounds and carbon. At temperatures less than 900 K and in the range of pressures from 3 to 22 GPa propane remains stable.

## Key words

Propane, high-pressure, DAC, Raman spectroscopy, IR spectroscopy, hydrocarbons

## Introduction

To the present day, hydrocarbon compounds attract scientific community from organic chemistry, geology and planetary sciences [1-3]. Hydrocarbons are of the great importance in the atmospheric processes of Earth [4], and giant planets [5,6], as well as their presence in the inner parts of the planets, is also of particular interest, especially in the deep carbon cycle [7-9]. Existence of hydrocarbon compounds in the wide range of pressures and temperatures is not a new phenomenon. In recent years, several papers related to the experimental study of the transformation of hydrocarbon systems under extreme thermobaric conditions corresponding to the Earth's upper mantle were published [2,10-12].

In most of these papers, the objects of research were complex hydrocarbon systems. The results of experimental studies of individual hydrocarbons were limited mainly to the study of methane and ethane [1, 13,14]. Despite the fact, that methane is a primary component of hydrocarbon systems both on the Earth and

other planets; other hydrocarbons are also presented and require careful, systematic research. Propane, the second homologue of methane, is a component of petroleum, natural gas and gas condensate. Its extra-terrestrial abundance was recently discovered in the atmosphere and lakes of Titan [15], Mars [16], Saturn [17]. Propane's abundance in various geological settings means the requirement of its high-pressure high-temperature study, which was conducted in a limited way only in few works [18], where only one phase transition at 3.2 GPa and ambient temperature was found. High-temperature experiments of propane were performed without the high-pressure influence and mainly for the development of industrial petrochemical processes such as pyrolysis and catalytic cracking [19,20]. In the high-pressure research of hydrocarbons, several significant findings were observed. For example, methane reaction at high pressures and temperatures could produce graphite or diamond [13,21], soot [22], hydrogen [23], heavier hydrocarbons like ethane, propane and butanes or even heavier [1]. Ethane reacts in two directions – it polymerizes with the formation of its heavier homologues as well as it decomposes to methane or carbon in various forms [24]. Understanding the physicochemical processes occurring in the deep layers of the Earth is impossible without information on the transformation of individual hydrocarbons under these conditions.

In this study, we have continued the series of experimental investigation of the transformation of individual hydrocarbons that began in [24]. We attempted to investigate propane molecule using diamond-anvil cell techniques (DACs) from two angles – in a high-pressure region without the influence of the temperature up to 40 GPa as well as with both high pressures and temperatures in a range of 2-22 GPa and 900-3000 K.

## **Methods**

### *Sample preparation*

Propane of 99,99 % purity (Linde Gaz Polska) was used during the investigation without further purification. With the help of cryogenic loading by liquid nitrogen, propane was liquefied and then loaded to symmetrical BX-90-type diamond anvil cells (DAC) equipped with synthetic, CVD-type IIa diamonds with a culet size of 250  $\mu\text{m}$ . For the high-pressure study at ambient temperature, the rhenium gasket was indented to a thickness of 35  $\mu\text{m}$  where the hole of 110  $\mu\text{m}$  in diameter was drilled by a laser technique to create a cylindrical sample chamber. To study the behaviour of propane at high pT conditions, a set of rhenium gaskets was prepared using laser ablation to create a place for a heater (gold foil with the thickness of ~1-2  $\mu\text{m}$  and 80  $\mu\text{m}$  in diameter). The laser ablation was performed to avoid contact between the

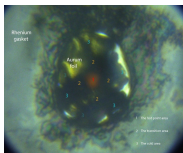
gold foil and the diamond. The cylindrical chamber was drilled in the ablated area (diameter 60  $\mu\text{m}$ ) in order to load the propane.

#### *Raman and Infrared spectra measurements*

The primary method of analysis in this study was Raman spectroscopy providing a particular number of Raman spectra, obtained by exciting of a He-Ne laser (632.8 nm excitation, 0.002 Wt) with acquisition by a LabRam spectrometer with a 2  $\text{cm}^{-1}$  spectral resolution. The low level of the laser power prevented possible photochemical reactions of hydrocarbons in the cell at extremely high pressures [25]. The high-pressure behaviour of propane was carefully analyzed to create a calibration between the value of pressure and the Raman shift of propane's vibrational modes. To measure the pressure, a tiny ruby chip with a size of  $\sim 3\text{--}5\ \mu\text{m}$  in diameter was placed near the centre of the drilled hole. To measure the pressure in the cell during HPHT experiments, a calibration obtained during the HP experiments was used. To provide reproducibility of the results the IR spectroscopy was employed using a Bruker Vertex80v FTIR spectrometer coupled to an IRscopeII microscope (Bruker Optics, Ettlingen, Germany) and equipped with an MCT detector at the ANKA Synchrotron Facility in Karlsruhe, Germany. The spectral resolution was set to 2  $\text{cm}^{-1}$ . The resulting IR spectra were analyzed using OPUS v7.2.139.1294 software. The uncertainties both in the Raman and IR peak positions were  $\pm 1\ \text{cm}^{-1}$ . To determine the hysteresis value, the pressure in the cell was measured twice before and after the spectra collection. To see the difference of propane high-pressure behaviour two sets of experiments were made – both for compression and decompression. For HPHT experiments, the Raman spectra were collected in various areas of the chamber – both in cold and hot sample areas (figure 1).

#### *Heating of the sample*

To heat the sample, the laser heating technique was applied in the presented investigation. Two YAG lasers with 1064 nm central wavelength were employed for this purpose. The temperature measurements the thermal emission spectra of the heated area is guided into an IsoPlane SCT 320 spectrometer with a 1024x256 PI-MAX 4 camera. For the determination of the temperature, the fitting of the black body radiation spectra of the heated area in a given wavelength range (570–830 nm) to the Plank radiation function was performed. Because of propane's optical transparency and low absorption at the central wavelength of the YAG laser, the gold foil was placed in the ablated area of the gasket (figure 1). The second relevant function of the gold foil, which explains its choice for the particular study is the low catalytic effect of Au on the hydrocarbon transformations.



**Figure 1.** The photo of the DAC sample chamber with the technique of collecting Raman spectra after performing of laser-heating experiment.

## Results and discussion

To the present day, vibrational spectroscopy, mainly Raman and IR, are widely used in geosciences. Vibrational spectroscopy allows the non-destructive investigation of the materials under extreme thermobaric conditions while being coupled with diamond-anvil cells. With the usage of Raman\IR + DAC pair, several hydrocarbons were examined in various ranges of pressures [26-31]. However, the knowledge about propane high-pressure behaviour even at ambient temperatures is limited. Only one liquid-solid phase transition at 3.2 GPa was detected using XRD by Podsiadlo et al. [18]. Study of high-temperature transformations of propane at high pressures was never performed. At the same time, the existing materials are focusing more on computational studies and assumptions based on methane and ethane high pressure-high temperature (HPHT) behaviour.

### *High-pressure behaviour of propane at ambient temperature*

Propane as a molecule has 27 vibrational modes and its spectral behaviour at ambient conditions was studied more than a half century ago [32-35]. Linear

alkanes due to strong similarities in structure have the same spectral properties – spectra of typical n-alkane could be divided in several regions:

- a) C-C skeletal stretching modes with the vibrations  $\sim 870\text{ cm}^{-1}/1057\text{ cm}^{-1}$  in the case of propane;
- b)  $\text{CH}_3$  and  $\text{CH}_2$  bending modes  $1400\text{-}1500\text{ cm}^{-1}$ ;
- c) Methyl ( $\text{CH}_3$ ) and methylene ( $\text{CH}_2$ ) stretching modes  $2800\text{-}3200\text{ cm}^{-1}$ .

To reveal the phase transitions of propane, it is necessary to see the certain change of Raman or IR spectra. In this work the pressure dependence of the propane's vibrational modes was studied in the range of 5-40 GPa. The main results which are corresponding to the phase transitions of propane and its vibrational modes under high pressure could be seen on the figure 2.



The usage of DAC's combined with Raman spectroscopy gives a significant drawback while investigating hydrocarbon behaviour due to the domination of diamond's first-order peak at 1200-1400  $\text{cm}^{-1}$ , where some of the hydrocarbon's bands are presented. The second-order diamond peak at 2100-2700  $\text{cm}^{-1}$  dominates throughout the region; however, no essential modes in the case of propane are known in this part of the spectrum. Another problem is a vast Rayleigh background which makes the observation of modes below 300  $\text{cm}^{-1}$  quite tricky even at high resolutions. In the case of IR spectroscopy, the region of 1800-2650  $\text{cm}^{-1}$  (two-phonon spectrum of the diamond) was eliminated from the spectra. Detailed descriptions of the phase transitions, pressure-vibrational modes correlations and collected IR and Raman spectra are available at [36].

### *Behaviour of propane in HPHT region*

The molecule of propane remains stable and untouched at the ambient temperatures and pressures up to 40 GPa, proposing a new idea of propane's investigation to the side of temperature influence on its structure.

The hydrocarbons' high-temperature reactions were studied in detail [37-39] for the development of industrial processes of propane's pyrolysis. While being exposed to the high temperatures (generally in the range of 600-1200 °C), propane is involved in a free-radical chain reaction with the formation of lighter gases, mainly ethylene, propylene and acetylene [39]. During the industrial process, one of the main aims is to keep the pressure as low as possible. The pressure's increase gives a start to the secondary reactions with the formation of tar-like products of highly aromatized compounds. During the propane's pyrolysis carbon in the form of soot and hydrogen are also typical constituents of products mixture [37-39].

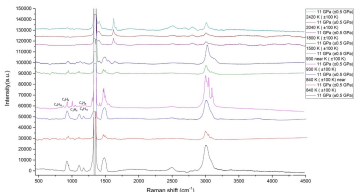
HPHT studies of propane homologues show quiet controversial results – some of them are proposing for methane and ethane only the decomposition reactions with the formation of carbon and hydrogen without any intermediate products [40,41]. However, some of the research groups report the formation of a broad range of products, indicating the positive influence of the high pressure on the length of the hydrocarbon chain. Computational studies of Ancilotto et al. [42] shows that the polymerization of methane could occur at 100 GPa and 4000 K with the formation of C2-C3 hydrocarbons with hydrogen. At the same time, the pressure increase till 300 GPa induces the polymerization more with the formation of long-chained hydrocarbons. In another report, Spanu et al. [43] using the molecular dynamics simulation provides us with more relevant data to the low-pressure region. It has shown that higher alkanes are stable in the range of 1000-2000 K and pressures  $>4$



GPa, which is also in a good agreement with the DAC-experimental work of Kolesnikov et al. [24].

In this part of the presented research, propane was investigated in the pressure range of 3-22 GPa in the temperature interval of 900-3000 K.

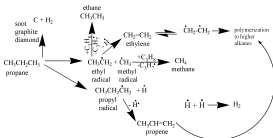
At any pressure, hydrocarbon compounds were detected on the spectra. Unfortunately, Raman spectroscopy is not the most effective tool for analysis of hydrocarbon mixtures due to the similarity of spectral representation of hydrocarbons from one group. However, using Raman spectroscopy could help to identify the class of compounds, the presence of elemental carbon or hydrogen. Raman spectroscopy could also solve the question of hydrocarbon stability under extreme conditions. It was found that propane remains stable at any pressure (3,6,8,11,14,17 and 22 GPa) at the temperatures up to ~900 K. The most informative spectra which were obtained during the current investigation are the spectra recorded at 11 and 14 GPa (figures 3 and 4 respectively).



**Figure 3.** Chemical transformations of propane at 11 GPa and  $T = 840\text{--}2420\text{ K } (\pm 100\text{ K})$ . The reference peaks for C-H valence of saturated hydrocarbon compounds were taken from [39-41], for unsaturated – from [42,43], for graphite (soot) modes were taken from [44,45]. The reference peaks for C-C stretching and C-C bending of hydrocarbons were taken for ethane from [23], for propane from [23,36], for n-butane from [23,46], for n-pentane [47], for n-hexane[48]. The propane remained stable at 840 K and less. The spectra of untouched propane are in good correspondence with the previous experiments made by us [36].

As it could be seen from the spectra (figures 4 and 5) after heating the propane higher than ~900 K we could indicate a dramatic change in the vibrational mode characteristics. Mixture of linear alkanes including ethane, butane, pentane (figure 4) and hexane (figure 3) is clearly could be recognized on the spectra. These results

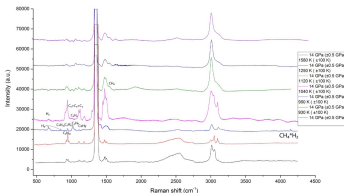
are in the well agreement with early work of Kolesnikov et. al [24] where behaviour of ethane was described in the same HPHT interval. Propane heating at extreme pressure leads to the formation of lighter and higher hydrocarbons, which accepts well-known mechanism of pyrolysis, where the part of propane molecules are destructed by severe HPHT conditions producing lighter alkanes and the other part is involving into the polymerization and condensation-like reactions:



Certain regularity of hydrocarbon peaks on the Raman spectra which are decreasing in intensity with the consequent increase of the molecular mass could also accept the idea of radical mechanism of this reaction. Modifying the reaction, proposed by Kolesnikov et. al [24] we could gain a following scheme:



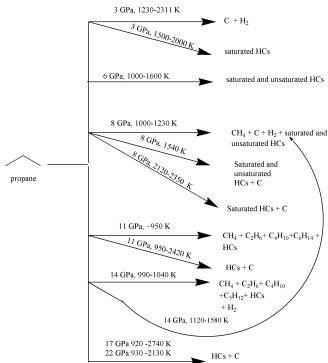
This reaction also supports the idea of the equilibrium state due to contemporaneous presence of hydrogen, graphite and other hydrocarbons. With the following temperature increase, it is hard to distinguish the particular hydrocarbon signal. After 1500 K only graphite and C-H valence vibrations were detected on the spectra.



**Figure 4.** Chemical transformations of propane at 14 GPa and  $T = 930\text{--}1580\text{ K}$  ( $\pm 100\text{ K}$ ). The reference peaks for C-H valence of saturated hydrocarbon compounds were taken from [39–41], for unsaturated – from [42,43], for graphite (soot) modes were taken from [44,45]. The reference peaks for C-C stretching and C-C bending of hydrocarbons were taken for ethane from [23], for propane from [23,35], for n-butane from [23,46], for n-pentane [47], for n-hexane[29]. The propane remained stable at 840 K and less. The spectra of untouched propane are in good correspondence with the previous experiments made by us [36].

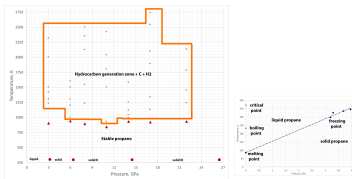
More Raman spectra with all of the vibrational modes that appeared during the transformations could be found in the appendix of this paper (figures A1–A5). Figure 5 below demonstrates the overview of the experiments carried out during the presented research. Without any catalytic material propane while being exposed under extreme thermobaric conditions could form both saturated and unsaturated hydrocarbons as well as molecular carbon, presumably in the form of graphite or soot with molecular hydrogen. That means that in the region of high pressures, the mechanism of pyrolysis could partially describe the HPHT of propane with two competing mechanisms of the reactions:

- 1) elongation of hydrocarbon chain via polymerization, cyclization or condensation reactions or cleavage of C-C and C-H bonds leading to the formation of lighter hydrocarbons;
- 2) destruction of the molecule to carbon in various forms and molecular hydrogen.



**Figure 5.** The schematic representation of the obtained results based on collected Raman spectra (HCs – hydrocarbons).

Taking into the consideration both sets of high-pressure experiments it became possible to expand significantly the phase diagram of propane from Podsiadlo et. al work (figure 6) [18].



**Figure 6.** Phase diagram of propane. The phase diagram shows the boiling and melting points at 0.1 MPa with temperatures of 231 and 86 K, respectively. The critical point of propane is also shown in the figure, 4.25 MPa (369.8 K). The freezing points on the 295 K line were obtained from the DAC experiments of Podsiadło et. al [18]. With propane optical observations, spectroscopic pressure calibration, and thermocouple temperature measurements, the blue freezing line was plotted with the melting point value at 0.1 MPa and 86 K, the freezing point at 3.20 GPa and 295 K, and the melting points at 3.30, 3.69, and 3.96 GPa with the corresponding temperatures. With Raman spectroscopy and laser-heated DAC used in the current research, the hydrocarbon generation zone was determined with the zone of propane stability as well as the existence of several solid phases of propane.

## Conclusion

High-pressure, high-temperature study of propane reveals new information concerning its behaviour under extreme thermobaric conditions. With the help of Raman and IR spectroscopic study of propane at the ambient temperature and pressures in the range from 3.6 (5) to 40 (5) GPa it was found that propane undergoes three solid-solid phase transitions at 6.4(5) (7.0(5) for IR) GPa, 14.5(5) (14.0(5)) GPa and 26.5(5) (27.0(5)) GPa respectively. The observation of these phase transitions supports the idea of no correlation between the molecular mass of hydrocarbon and the number of phases. The behaviour of vibrational modes of propane has a strong correlation with the pressure increase and acts in the same way as in the case of other linear hydrocarbons. As for the investigation of the temperature role in the high-pressure behaviour of propane, it was revealed, that  $C_3H_8$  remains stable at 3-14 GPa and <900 K, while with the temperature rise the mixture of various hydrocarbons species was formed with the presence carbon in the form of soot or graphite. It was shown that heavier alkanes could be produced from propane in the broad range of temperatures ( ~1000-2000 K) and pressures (3- 22 GPa) without any catalytic materials locked in the DAC chamber.

## Author contributions

V.K. created the concept of the study. D.K. with the help of L.D. has made all of the experiments. The obtained data was analyzed by D.K. The paper was written by D.K. with essential help of L.D. and V.K. All of the figures and schemes were drawn by D.K. The materials and all of the necessary laboratory equipment were provided by L.D.

### **Acknowledgments**

We thank A. Kurnosov for valuable information and comments during experiments. We thank E. Koemets for the help in performing of cryogenic loading of propane. We are also grateful to T. Fedotenko for the laser-heating of propane sample.

We thank E. Mukhina, D. Simonova, D. Druzhbin, S. Chariton, L. Ismailova, S. Khandarkhaeva, Y. Koemets for providing their advice during the whole investigation. We highly appreciate the help of N. Dubrovinskaia while organizing the high pressure experiments at ANKA. We also gratefully acknowledge the IBPT for provision of instruments at the IR2 beamline at ANKA and M. Süpfle for his assistance.

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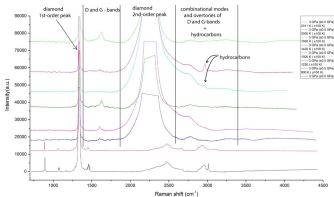
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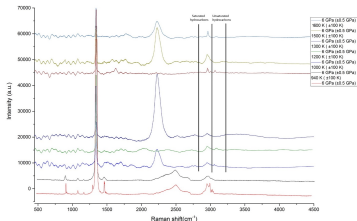
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## Appendix

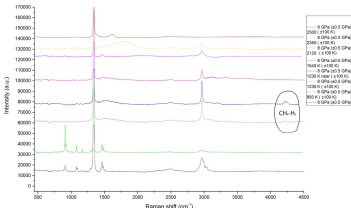


**Figure A1.** Chemical transformations of propane at 3 GPa and  $T = 900\text{--}2311\text{ K } (\pm 100\text{ K})$ . The spectra of untouched propane are in good correspondence with the previous experiments made by us [36].

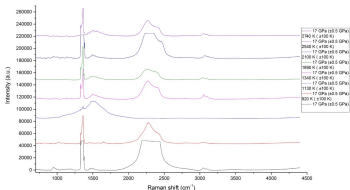


**Figure A2.** Chemical transformations of propane at 6 GPa and  $T = 940\text{--}1600\text{ K } (\pm 100\text{ K})$ . The strong fluorescence in the region of hydrocarbon footprint is explained by precision of complex

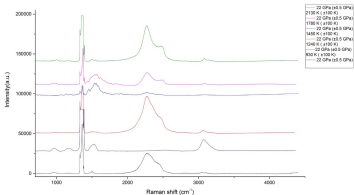
hydrocarbon systems of mixed structure. The formation of ultradispersive diamonds could also affect the spectra. The propane remained stable at 940 K. The spectra of untouched propane are in good correspondence with the previous experiments made by us [36].



**Figure A3.** Chemical transformations of propane at 8 GPa and  $T = 893\text{--}2500\text{ K}$  ( $\pm 100\text{ K}$ ). The strong fluorescence in the region of hydrocarbon footprint is explained by the precision of complex hydrocarbon systems of mixed structure. The possible formation of ultradispersive diamonds could also affect the spectra. The propane remained stable at 893 K. The spectra of untouched propane are in good correspondence with the previous experiments made by us [36]. The complex methane-hydrogen compounds reference peaks were taken from [32].



**Figure A4.** Chemical transformations of propane at 17 GPa and  $T = 920\text{-}3100$  K ( $\pm 100$  K).



**Figure A5.** Chemical transformations of propane at 22 GPa and  $T = 930\text{-}2130$  K ( $\pm 100$  K).