The role of deep hydrocarbons in the global hydrocarbon budget

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Abstract

Nowadays, the issue of global warming and related environmental problems is the object of widespread awareness within the scientific community, the political sphere, industry as well as affecting our everyday lives. Such a negative impact on the atmosphere is attributed mainly to human activity. It is thought that one of the most dangerous greenhouse gases is carbon dioxide (CO₂). Nevertheless, the problem of hydrocarbon emissions began to receive particular attention due to the exponential growth of methane emissions in the atmosphere. What is the reason for such behavior and what about other hydrocarbons, especially, ethane, propane and butane isomers?

In this study, it was proposed that geological emissions, mainly the emission from the dissociation of natural gas hydrates is one of the main reasons for the dramatic rise in hydrocarbon emissions into the atmosphere. Natural gas hydrates are not only composed of methane and water cages but have in their structure a broad range of hydrocarbons, including ethane, propane, butanes. The purpose of this thesis is to investigate the sources of non-methane volatile hydrocarbons in the atmosphere, examine their impact on the environment and explore the correlation of hydrocarbon emissions with CO₂ emissions.

To reveal the impact of natural gas hydrates on the hydrocarbon budget it was assumed that hydrocarbons that are contributing to the natural gas hydrate formation have deep mantle origin. To confirm this hypothesis, high-pressure high temperature investigation of propane and butanes were conducted. The results of this investigation are presented in this thesis. To model extreme thermobaric conditions, the diamond-anvil cell technique with two-sided laser heating was used. The method of Raman spectroscopy was applied in the analysis.

The results obtained show that propane and butanes are stable in the pressure range 3-22 GPa at ambient temperature. Propane remains stable at temperatures up to 900 K. At temperatures >900 K chemical transformations of propane start to occur producing a mixture of light alkanes.
Keywords
Hydrocarbons, non-methane volatile hydrocarbons, carbon dioxide, methane, ethane, propane, butane, global warming, diamond-anvil cells, Raman spectroscopy, high pressure, high temperature, phase transition.
Abstrakt

I dagens samhälle har global uppvärmning och relaterade miljöproblem blivit en högst aktuell fråga inom vetenskap, politik, näringsliv samt påverkat vår vardag på individnivå. Den huvudsakliga anledningen till den negativa påverkan på atmosfären tillskrivs mänskliga aktiviteter. Man tror att en av de farligaste växthusgaserna är koldioxid (CO2). Ändå har problemet med kolväteutsläpp fått särskild uppmärksamhet på grund av den exponentiella tillväxten av metanutsläpp i atmosfären. Vilka är orsakerna bakom detta fenomen, samt hur står det till med andra kolväts påverkan: etan, propan och butanisomerer?

En huvudhypotes i denna avhandling är att geologiska utsläpp, främst utsläpp som har att göra med dissociation av naturgashyrdrat, är en av de främsta orsakerna till den dramatiska ökningen av kolväteutsläpp till atmosfären. Naturgashyrdrater består inte bara av metan- och vattenburar, utan har ett brett spektrum av kolväten (inklusive etan, propan, butaner och några andra) i sin struktur. Syftet med denna avhandling är att undersöka källor till flyktiga icke-metan kolväten i atmosfären, samt undersöka deras påverkan på miljön och undersöka korrelationen mellan kolväteutsläpp och koldioxidutsläpp.

För att avslöja effekterna av naturgashyrdrater på kolvätebudgeten, antogs det i denna avhandling att kolväten som bidrar till naturgashyrdratbildningen har sitt ursprung i djupmanteln. För att bekräfta denna hypotes genomfördes en högtrycksundersökning av propan och butaner under hög temperatur. Resultatet av undersökningen presenteras i denna avhandling. För att modellera extrema termobariska förhållanden tillämpas en diamant-städcellt teknik med dubbelsidig laseruppvärmning. I analysen till-lämpas metoden för Raman-spektroskopi.

Resultaten visar att propan och butaner är stabila i tryckområdet 3-22 GPa vid omgivningstemperatur. Propan förblir stabil vid temperaturer upp till 900 K. Vid temperaturer> 900 K börjar kemiska transformationer av propan att ge en blandning av lätta alkaner.
Nyckelord
Kolväten, flyktiga kolväten som inte är metan, koldioxid, metan, etan, propan, butan, global uppvärmning, diamant-städceller, Raman-spektroskopi, högt tryck, hög temperatur, fasövergång
Preface

This thesis is dedicated to the chemical behavior of propane and butanes and their role in the formation of natural gas hydrates.

The thesis is divided into four chapters.

The introduction (chapter 1) is devoted to the non-methane volatile hydrocarbons (NMVHCs) and their role in the atmosphere, the dissociation of natural gas hydrates and their contribution to the hydrocarbon budget as well as the correlation between CO\textsubscript{2} and hydrocarbon emissions. This chapter also describes the high-pressure behavior of hydrocarbons and the current state of the research. The main aim of the research and some additional objectives are also presented in the introduction chapter.

The chapter entitled “Methods” (chapter 2) provides a thorough description of the methods and experimental procedures used during this thesis, including Raman spectroscopy, diamond-anvil cell techniques, and the cryogenic loading method.

Chapter 3 deals with the phase behavior of propane and butane isomers at pressures of up to 40 GPa and ambient temperatures which were investigated using diamond-anvil cell techniques combined with Raman spectroscopy. Here the vibrational modes of propane and butanes were analyzed in terms of increasing pressure with the consequent phase transitions at the particular values of pressures.

Chapter 4 reveals the high-pressure, high-temperature transformations of propane, focusing on the mechanisms of transformations and the Raman spectroscopy analysis of the obtained products.
Acknowledgements

The first person who I would like to thank is my scientific supervisor, Vladimir Kutcherov. Vladimir showed me the world of science, made it possible for me to study in one of the best European universities and helped me with all of the problems which occurred during my PhD studies. Under the guidance of my supervisor I developed both my professional skills and different personal traits of character. I will never forget the opportunity that was provided by Vladimir.

My scientific team also gave me a lot of necessary information and shared their experience with me – thanks to Elena, Anton and Aleksandr for creating such a friendly atmosphere in our laboratory. I also want to express my appreciation to Elena, who became a close friend to me during these years.

Another scientific team which helped me to grow as a professional scientist is the team from Bayreuth Geological Institute in Germany, especially the group of talented scientists under the guidance of Leonid and Nataliya Dubrovinsky – Egor, Leila, Sayana, Timofey, Yuliya, Dariya, Stella, Irina as well as Alexandr Kurnosov, Dmitriy and other members of BGI. These people became a second scientific family to me.

I would like to thank the Department of physics at Gubkin University, especially the Head of the Department, Alexey Chernoutsan for providing the basis for performing the unique experiments.

Furthermore, last but not least I would like to thank my family and friends. These people were with me during my studies, they helped me financially, morally, they healed me from my depressions, and they cooked me dinners when I had no time to do it myself; they helped me in many ways. I will never forget this. My mother, Nadezhda, is the main person whose care and aid gave me the strength to finish everything on time and not to fail. I also want to thank my friends for everything, especially Yuliya, Igor, Serafima, Elena, Dmitrii, Madina, Mariya, Tatiana, Anna and Irina.

Stockholm, February 2020

Daniil A. Kudryavtsev
List of appended papers

Paper A

Paper B

Paper C
D. Kudryavtsev, T. Fedotenko, E. Koemets, S. Khandarkhaeva, V. Kutcherov, L. Dubrovinsky Chemical transformations of propane at extreme pressures and temperatures, accepted

Paper D
D. Kudryavtsev, A. Serovaikii, L. Dubrovinsky, V. Kutcherov High-pressure chemistry of propane, submitted

Related publications

V. Kutcherov, A. Kolesnikov, E. Mukhina, A. Serovaiky, Teaching aid “High-pressure high-temperature experimental studies”, Gubkin Russian State University of Oil and Gas (National Research University), 2016;
E. Mukhina, A. Kolesnikov & V. Kutcherov, The lower pT limit of deep hydrocarbon synthesis by CaCO₃ aqueous reduction, Scientific Reports, 7 (5749), 2017, doi:10.1038/s41598-017-06155-6
Authors’ contributions

The objectives of the project were developed by Daniil Kudryavtsev under the guidance of the main supervisor associate professor Vladimir Kutcherov. Daniil Kudryavtsev performed all experiments and data analyses described in the present thesis. Daniil Kudryavtsev wrote all texts for all appended papers, and as the corresponding author for all papers, prepared and revised them for publication after co-authors’ advises and comments.
Definition of critical terms and nomenclature

*Radiative (climate) forcing* - the difference between insolation (sunlight) absorbed by the Earth and energy radiated back to space.

*Seepage* - the process of relatively slow escape of a petroleum or natural gas through porous material or small holes. *Macroseepage* - visible oil and gas seeps; located at faults, fractures, and outcrops. *Microseepage* – not visible but detectible; occurs above mature source rocks and over accumulations.

*RedOx conditions* – conditions, specified by the tendency of the environment to be oxidized or reduced.

**List of abbreviations**
- DAC – diamond anvil cell
- LRV – large reactive volume
- NMVHCs or NMHCs – non-methane (volatile) hydrocarbons
- C – carbon
- CO₂ – carbon dioxide
- CH₄ – methane
- C₂H₆, C₃H₈, C₄H₁₀ – ethane, propane and butanes
- HPHT – high-pressure high temperature

**List of notations**
- V – volume
- m – mass
- ρ – density
- M – molar mass
- n – amount of substance
- P – pressure
- T – temperature
- 2θ – diffraction angle
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Chapter 1. Introduction

This thesis follows the investigation of the role of deep hydrocarbons in the formation of natural gas hydrates. The source of gas hydrates remains unclear, while the increase in the surface temperature leads to the hydrate decomposition and the ensuing release into the atmosphere of C$_1$-C$_4$ alkanes. While moving to the troposphere, C$_1$-C$_4$ alkanes are removed by the complicated mechanism of oxidation. This process results in the extra amount of CO$_2$ in the atmosphere. The study of hydrocarbon formation in the deep interior of the Earth, as well as the behavior of light hydrocarbons within the particular thermobaric conditions of the Earth's mantle, will help to complete the puzzle of the global CO$_2$ budget and the global carbon cycle. The central part of this PhD dissertation places the focus upon the high-pressure high-temperature modeling of hydrocarbon synthesis and its transformations, which could affect the atmospheric concentrations of CO$_2$ in a certain way.

1.1. Hydrocarbons emissions

Today, the increase in hydrocarbon emissions into the atmosphere is a growing problem in society, politics and science. The focus on the role of CO$_2$ emissions has overshadowed the problem of hydrocarbon compounds. Hydrocarbons have a substantial impact on the atmosphere. Emissions of hydrocarbons, mainly methane and its closest homologues (ethane, propane and butanes) lead to a complex series of chemical, physical or physico-chemical transformations with the formation of ozone in urban and regional areas\(^1\) as well as in the global troposphere\(^2\). Other problems which are caused by hydrocarbon emissions are acid deposition\(^3\), the formation of secondary particulate matter through gas/particle partitioning of
both emitted chemical compounds and the atmospheric reaction products of volatile organic compounds\textsuperscript{4-7}. Hydrocarbons are a special group of volatile organic compounds (VOCs), primarily, due to their relatively low chemical reactivity and consequently high ambient mixing ratios. Methane is an active greenhouse gas, a significant component of natural gas systems as well as the most abundant hydrocarbon on the Earth and in the solar system. However, other saturated hydrocarbons, such as methane, have not been investigated. This group is often called non-methane hydrocarbons and is also present in the Earth’s atmosphere and geological settings.

Ethane, propane, iso- and normal butanes (branched and linear) are standard components of petroleum and petrochemical systems, such as crude oil, refinery gases or natural gas hydrates\textsuperscript{8}. Why are these compounds so important? The atmosphere of the Earth is changing at a rapid rate due to emissions of these VOCs. Volatile organic compounds are always attributed to human activity and the development of the industrial and transportation sectors. The chemical composition of the atmosphere changed dramatically over the last 100 years affecting the Earth’s climate and biosphere. The role of CO\textsubscript{2}, nitrogen oxides, freons as well as methane is well-known and has been investigated from different angles in more than a thousand publications by scientists\textsuperscript{9-12}. With the results of several studies\textsuperscript{13-14}, it has become evident that significant concentrations of light alkanes or non-methane volatile hydrocarbons (NMVHCs) are present in the global troposphere. While the role of methane as the main greenhouse component has been studied for over two decades\textsuperscript{15-18}, interest in other alkanes is relatively new. These hydrocarbons are expected to play a specific role in the chemistry of the atmosphere. Non-methane volatile hydrocarbons are relevant trace components of the atmosphere, especially at its lower layers\textsuperscript{19}. Ethane, propane and butanes have always been chemically and physically associated with methane. They could possibly be released into the atmosphere via the same pathways as methane – oceans\textsuperscript{20}, vegetation on land\textsuperscript{21} and via anthropogenic activity, including emissions from vehicles
and aircraft, solvent use and its production, and also via the distribution and combustion of fossil fuels\textsuperscript{22} or biomass burning\textsuperscript{23}. Another question is how these compounds could be distributed in the atmosphere – even ethane, the second member of the alkane homologous series, is heavier than air. However, hundreds of studies made using balloons, aircraft or satellites\textsuperscript{24-27}, have shown the presence of various organic compounds in the atmosphere, including, for example, decane ($C_{10}H_{22}$), which is seven times heavier than air. All of the most abundant hydrocarbons in the universe - ethane, propane, butane, pentane, hexane isomers, as well as branched alkanes and aromatic compounds were found in the atmosphere\textsuperscript{14,21,23}.

The occurrence of vast amounts of hydrocarbons in the atmosphere could be explained in the following way: the atmosphere is not stagnant, which means that winds mix the atmospheric compounds at altitudes far above the stratospheric levels much faster than these molecules can settle according to the gravitation forces. Gases do not separate in the atmosphere by their weight. The time estimation of diffusional stratification of gases is more than a thousand years, and in the dynamic atmosphere, it is impossible. With the processes of turbulence, vertical mass-transfer and convection gases makes in the layers below turbopause\textsuperscript{28}.

Light alkanes are relatively inert in the lower part of the atmosphere. They could migrate to its upper parts due to convectional flows regardless of their molecular weight. The abundance of hydrocarbons (as well as other organic compounds) decreases with the higher altitude, where they could be broken down by ultraviolet radiation. Even if the gas mixing did not exist, the layers of CO\textsubscript{2} or argon with the thickness of 10 km would appear, making the Earth's surface uninhabitable.

Over the years, among the scientific society, it was thought that emissions of light hydrocarbons into the atmosphere where linked to anthropogenic activity. Nevertheless, during the last decade, the results of Etiope's study\textsuperscript{29} showed that one of the primary sources of these emissions is geological.
Historically, light hydrocarbons have been associated with methane and anthropogenic emissions. The estimates of hydrocarbon emissions were mainly based on the assumptions that the dominant source is linked to industrial processes, such as venting and flaring of fossil fuels, biomass burning, air leaks during natural gas extraction and distribution. The geological emissions of methane and non-methane hydrocarbons have only recently started to be considered. The reason why geological emissions have not been investigated in detail is the high degree of uncertainty concerning the magnitude of this contribution. Geological sources are often not included in estimates of net emissions and consequently neglected. For example, in this study\textsuperscript{29} it is stated, that global levels of ethane and propane in the atmosphere have been underestimated by more than 50%. Moreover, their emissions, atmospheric distribution, and trends in their atmospheric concentrations are insufficiently understood. It is thought that since preindustrial times, atmospheric ethane and propane concentrations in the Northern Hemisphere have increased by a factor of 3–4, mainly due to fossil fuel emissions\textsuperscript{30}. After a period of decline between the 1970s and 2005\textsuperscript{19, 31}), ethane concentrations have picked up again\textsuperscript{32}.

There is still uncertainty over why all NMVHCs emissions of unknown origin are attributed to the anthropogenic source? Atmospheric chemistry models generally underestimate present-day concentrations and emissions of ethane and propane\textsuperscript{30,33,34}.

Natural gas is a mixture of explosive and toxic compounds, which also have strong greenhouse potential and are the cause of photochemical pollution in the atmosphere. Consequently, natural gas seepage and leakage to the Earth's surface and the atmosphere have several environmental implications. Recognizing the sources of emissions is a fundamental problem which could be solved only by the usage of proper detection techniques, combined with correct concepts and interpretative tools.
The contrast difference between hydrocarbons emissions studies could be explained not only by anthropogenic activity alone. It could be attributed to the processes of the Earth's degassing. Today, there is some evidence that the degassing of the Earth's mantle could be a significant contributor to the global emissions into the atmosphere.5,12

Knowledge of NMVHCs emissions is essential, but the more important question is how to understand the significance of these compounds in the lower layers of the atmosphere. NMVHCs could also be described with the well-known characteristics of greenhouse gases, such as global warming potential, lifetime period and radiative forcing. Comparative characteristics of five saturated hydrocarbons are presented in Table 1.1. The properties of ethane, propane and butanes were compared to the methane. The primary role of ethane, propane and butanes is their interactions with OH and Cl radicals, leading to photochemical pollution and ozone generation in the troposphere (see 1.1.1-1.1.3 reactions).35 That means that with the weak absorption and emission of longwave radiation these gases affect the atmospheric radiative balance indirectly - mainly as precursors of ozone (O₃), and through reaction with the hydroxyl radical (OH), which leads to less concentration of OH-radicals and thereby a longer atmospheric lifetime of methane (CH₄).

During this mechanism of oxidation, peroxy radicals are formed which contribute to ozone production on both local and regional scales.35,36 Ozone is a desirable gas in the stratosphere (in the stratosphere, ozone plays the role of blocker of sun's ultraviolet radiation). On the other hand, ground-level ozone acts like a greenhouse gas, harming ecosystems and human health. Elevated levels of NMVHCs (and other VOCs) and NOx (nitrogen oxides) have led to an approximate doubling of ozone in the lower troposphere over the past couple of centuries, making tropospheric ozone the third most abundant anthropogenic greenhouse gas followed by the carbon dioxide and methane.
Table 1.1 Comparative characteristics of NMVHCs

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Lifetime period</th>
<th>Total emissions, Tg/Year</th>
<th>Global concentration in atmosphere</th>
<th>Global warming potential over 100 years, GWP</th>
<th>Geological annual emissions, Tg/year</th>
<th>Indirect radiative forcing, mW/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane C₂H₆</td>
<td>2 months</td>
<td>13.57²⁹, 15.57²⁹, 19⁴⁴</td>
<td>0.5 ppb³², 0.4-2.5 ppb³²</td>
<td>10</td>
<td>2-4</td>
<td>1</td>
</tr>
<tr>
<td>Propane C₃H₈</td>
<td>2 weeks</td>
<td>12.01³³, 15-20²⁹, 23⁴³</td>
<td>0.3 ppb³²</td>
<td>10</td>
<td>1-2.4</td>
<td>0.9</td>
</tr>
<tr>
<td>n-Butane C₄H₁₀</td>
<td>5-6 days</td>
<td>14.1³⁵, 22.7⁴⁵</td>
<td>100-500 ppt³³</td>
<td>7</td>
<td>not reported</td>
<td>0.6</td>
</tr>
<tr>
<td>i-Butane C₄H₁₀</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methane CH₄</td>
<td>8.9±0.6 years³⁹ 12 years³⁹</td>
<td>720⁴¹</td>
<td>1866 ppb⁴⁰</td>
<td>28³⁹</td>
<td>42-64</td>
<td>-</td>
</tr>
</tbody>
</table>
Ethane or propane alone could not contribute all of the ozone's formation in the atmosphere. If we take into consideration that among the wide variety of volatile organic compounds in the atmosphere, the NMVHCs are the most representative group, their investigation from different sides becomes exceptionally urgent. Moreover, scientists need to understand accurately and precisely the levels of hydrocarbons in the atmosphere to predict the exposure of the population to ozone. Tropospheric ozone causes a variety of serious health complaints and along with particulate matter and nitrogen dioxide it is one of the three major causes of pollution-related deaths. Ozone also damages and stresses plants and various vegetation, which results in a reduction in terrestrial CO$_2$ sequestration. On the other hand, it is necessary to note that sources of NMVHCs are diverse and hydrocarbons could be emitted from more than 50 sources, both natural (geological, oceanic, forestry) and anthropogenic. With the information mentioned above, it may be concluded that NMVHCs emissions are also of concern for air quality and radiative forcing.

Ozone does not react with hydrocarbons directly, but rather creates the OH radical by the photolysis reaction (1.1.1). The reaction of ozone with hydrocarbons could be described as follows (1.1.2), where R is an alkyl group, $h\nu$ photon:

$$O_3 + h\nu = O_2 + O^\cdot$$

(1.1.1)

$$O^\cdot + H_2O = OH^\cdot + OH^\cdot$$

(1.1.2)

$$RCH_2\cdot - H \text{ (hydrocarbon)} + OH^\cdot = RCH_2\cdot + H_2O$$

$$RCH_2\cdot + O_2 = RCH_2O_2^\cdot \text{ (peroxy radicals)}$$

$$RCH_2O_2^\cdot \Rightarrow \text{aldehydes, ketones, esters... etc...} \Rightarrow \text{CO}_2 + H_2O$$

The proposed mechanism looks adequate and straightforward. However, in the atmosphere with more than a thousand compounds and different conditions, the real situation differs drastically. This mechanism means that due to the oxidation of NMVHCs in the atmosphere, more than a thousand compounds could be obtained.
Some of them do not pose a threat to the environment and living organisms, but some of them could exacerbate the negative processes in the troposphere.

The main problem is that ultimately, these compounds are transformed into CO\textsubscript{2} and H\textsubscript{2}O, which do play a crucial role in atmospheric processes. This means that despite the more than 20 sources of CO\textsubscript{2} at ground level, we have one more, unaccounted source of CO\textsubscript{2}, which could be called indirect or “double counting carbon”.

The phenomenon of indirect emissions occurs when one of the emitted compounds (in our case – five saturated hydrocarbons) affects the atmospheric burden of another greenhouse gas (carbon dioxide). From the chemical point of view, the oxidation (note, that this process is not combustion) process of 1 kg of methane provides 2.75 kg of CO\textsubscript{2}, while the oxidation of ethane, propane and butanes will release 2.93, 3.0 and 3.03 kg respectively (1.1.3):

\[
\begin{align*}
\text{CH}_4 + \text{O}_2 &= \text{CO}_2 + 2\text{H}_2\text{O} \\
2\text{C}_2\text{H}_6 + 5\text{O}_2 &= 4\text{CO}_2 + 6\text{H}_2\text{O} \\
\text{C}_3\text{H}_8 + 5\text{O}_2 &= 3\text{CO}_2 + 4\text{H}_2\text{O} \\
4\text{C}_4\text{H}_{10} + 21\text{O}_2 &= 16\text{CO}_2 + 10\text{H}_2\text{O}
\end{align*}
\]  

(1.1.3)

With simple calculations which may be seen in the Appendix, we have obtained the value of an extra 1.9 Gt of CO\textsubscript{2} (11 % of resulting CO\textsubscript{2}) which may be produced during the oxidation processes.

In the next chapter, the role of CO\textsubscript{2} emissions is described and the value of indirect CO\textsubscript{2} emissions is added to the global carbon dioxide budget.

1.2. Global carbon dioxide budget

The concentration of carbon dioxide (CO\textsubscript{2}) in the atmosphere has continuously risen since the 18th century. Today, the increase in CO\textsubscript{2} concentration looks almost dramatic – from 277 ppm in the middle of the 18th century to 415 ppm in 2019 (figure 1) \textsuperscript{46}. 

Nowadays, the fossil fuel emissions of CO2 are thought to be the main contributor to the change in the global CO2 budget and, therefore, global climate change. However, fossil fuel emissions are not the only source of emissions in the atmosphere; the existing scientific data provides us with additional CO2 sources and sinks, which have high variability and rely on different factors. For example, the main large carbon reservoirs, which act as the leading sinks of carbon - biosphere and ocean, are not «fixed», which means that measurement of CO2 emissions could also depend on the land or ocean size, geographical position, or type of the landscape.

*Figure 1.2.1* The change in average concentration of carbon dioxide over time (ppm/years)\(^{47-49}\). NOAA - National Oceanic and Atmospheric Administration, ESRL - Earth System Research Laboratory

CO2 emissions, being not accounted, could open the door for various abuses:

1) Inaccurate accounting;
2) False declaration of territory’s emissions;
3) Misleading demands for CO2 global budget, which are associated with clean development mechanisms as well as geological and engineering options;
4) Improper environmental policy regulations.

Understanding of the global carbon budget mechanism, correct evaluation of CO2 emission sources and sinks with underlying trends in natural and anthropogenic carbon cycling are the key to determined climate stabilization aims.
Figure 1.2.2 shows the global carbon budget modified from its basic characteristics, and besides them, it provides the causal links between different sources and sinks of CO2 with the addition of a new source of CO2 as represented by the oxidation process of hydrocarbons.

If the hydrocarbons are the source of CO2, that means that there could be a correlation between hydrocarbon emissions and CO2 emissions (fig. 1.2.3). The dynamical data of NMVHCs over the last five decades is not presented in the scientific literature. We could
assume that NMVHCs emissions have the same trends as methane while being correlated with CO2 emissions.

\[ \text{Figure 1.2.3. The correlation between methane and CO}_2\text{ concentrations in the atmosphere from 1983 to 2019. The data set for CO}_2\text{ was taken from 52, for CH}_4\text{ from 53 both from ESRL (https://esrl.noaa.gov).} \]

The main question there is why the growth of hydrocarbon emissions into the atmosphere has been so huge (figures 1.2.4, 1.2.5), especially in the last two decades. For example, over the last twenty years, there was no substantial change in petroleum exploration, wetland formation, agricultural fields. However, if the rise in methane concentrations could be partially explained by these factors (fig.1.2.4 – over the last decades and fig.1.2.5 – an overall graph showing the exponential growth of methane in the atmosphere), the atmospheric growth of C$_2$-C$_4$ hydrocarbons remains even more open to question. However, one accounted or
poorly accounted source of hydrocarbons in the atmosphere could explain the exponential growth of the average concentrations of methane, ethane, propane and butanes. This potential source could be natural gas hydrates, which are populated over large areas all over the world.

Figure 1.2.4. The growth of methane concentration in ppb (nmol/mol) in the atmosphere during the last 50 years. Starting from the 21st century the growth of hydrocarbon emissions became more abrupt.
Figure 1.2.5. Methane content in the atmosphere obtained from measurements in glaciers in Antarctic and Greenland and in environmental samples collected in Tasmania.

1.3. Natural gas hydrates and their role in the hydrocarbon emissions

At the present time, natural gas hydrates reserves are estimated in the wide range presented on Table 1.3.1. The conventional natural gas reserves are estimated as 13000 trillion m$^3$. But what does this amount of natural gas hydrates actually show? It means that total amount of organic carbon which occurs in natural gas hydrates all over the world is twice as high as that the amount of organic carbon from fossil fuels (fig. 1.3.1).
The precise estimation of natural gas hydrate reserves on the Earth is a challenging problem, which could be reflected by Table 1.3.1 below:

Table 1.3.1 The existing estimations of gas hydrate reserves.

<table>
<thead>
<tr>
<th>Permafrost hydrate</th>
<th>Marine hydrates/m³</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5.7 \times 10^{13}$</td>
<td>$5.25 \times 10^{14}$</td>
<td>Trofimuk, 1977</td>
</tr>
<tr>
<td>$3.1 \times 10^{13}$</td>
<td>$3.1 \times 10^{15}$</td>
<td>Melver, 1982</td>
</tr>
<tr>
<td>$3.4 \times 10^{16}$</td>
<td>$7.6 \times 10^{18}$</td>
<td>Dobrynin, 1981</td>
</tr>
<tr>
<td>$1.4 \times 10^{13}$</td>
<td>-</td>
<td>Meyer, 1981</td>
</tr>
<tr>
<td>$1.0 \times 10^{14}$</td>
<td>$1.0 \times 10^{14}$</td>
<td>Makogon, 1981</td>
</tr>
<tr>
<td>$7.4 \times 10^{14}$</td>
<td>$1.8 \times 10^{16}$</td>
<td>Kvenvolden, 1988</td>
</tr>
<tr>
<td>$2.1 \times 10^{16}$</td>
<td>$2.1 \times 10^{16}$</td>
<td>MacDonal, 1990</td>
</tr>
<tr>
<td>$(2.6 - 13.9) \times 10^{16}$</td>
<td>$0.38 \times 10^{15}$</td>
<td>Gornitz and Fung, 1994</td>
</tr>
<tr>
<td>$(0.38 - 1.0) \times 10^{15}$</td>
<td>$0.38 \times 10^{15}$</td>
<td>Ginsburg and Soloviev, 1995</td>
</tr>
</tbody>
</table>
Gas hydrates (clathrates) themselves are clathrate compounds, where the molecules of gas-guest are trapped in the crystalline cells of water. It is a well-known fact that gas hydrates may be formed from different types of gases, not only from methane. It depends on the thermobaric conditions of their formation and composition of the guest-molecule. In the case of methane and light-saturated hydrocarbons, they are formed when water and gas occur together at a relatively low temperature (up to 288 K) and high pressures (2-12 MPa). This means that the clathrate compounds could be formed, for example, in oil and gas wells or pipeline equipment. Natural gas hydrates could also be formed in nature – first of all, under the permafrost at a depth of between 0.5 and 1.2 km or in marine environments under the seafloor level at different depths. Natural gas hydrates are the example of metastable minerals, and among the temperature, pressure and chemical composition, their formation, stability and other properties may be affected by the chemical composition of the “environment” around – for example, the salinity of water or geological characteristics of the porous media. Despite the fact that the term “natural gas hydrate” is synonymous with the term “methane hydrate”, the real composition of a gas hydrate molecule is “flexible”, including other guest compounds such as carbon dioxide, nitrogen, hydrogen sulfide and light-saturated hydrocarbons, mainly ethane, propane and butane. The number of guests in the water cage depends on the pressure and temperature of their existence during the formation of the hydrate. Moreover, the processes of migration of gas-water mixture could affect the final composition. Usually, the composition of natural gas hydrates is described as methane constituted. However, there is much evidence of various gas hydrates composition with a dramatic increase in heavy hydrocarbon content (Table 1.3.2, Table 1.3.3).


Table 1.3.2 Composition of gas of natural gas hydrates

<table>
<thead>
<tr>
<th>Gas hydrate deposit</th>
<th>Gas composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH₄</td>
</tr>
<tr>
<td>Haakon Mosby Mud volcano</td>
<td>99.5</td>
</tr>
<tr>
<td>Nankai Trough, Japan</td>
<td>99.3</td>
</tr>
<tr>
<td>Bush Hill White</td>
<td>72.1</td>
</tr>
<tr>
<td>Bush Hill Yellow</td>
<td>73.5</td>
</tr>
<tr>
<td>Green Canyon White</td>
<td>66.5</td>
</tr>
<tr>
<td>Green Canyon Yellow</td>
<td>69.5</td>
</tr>
<tr>
<td>Bush Hill</td>
<td>29.7</td>
</tr>
<tr>
<td>Messoyakha, Russia</td>
<td>98.7</td>
</tr>
<tr>
<td>Mallik, Canada</td>
<td>99.7</td>
</tr>
<tr>
<td>Nankai trough-1, Japan</td>
<td>94.3</td>
</tr>
<tr>
<td>Blake ridge, USA</td>
<td>99.9</td>
</tr>
</tbody>
</table>
Table 1.3.3 The average gas hydrate content.

<table>
<thead>
<tr>
<th>Gas hydrate composition</th>
<th>Average range of content (%) and the size of representation (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>46.01-99.99 (n=230)</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>0 – 15.37 (n=230)</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>0-21.05 (n=230)</td>
</tr>
<tr>
<td>i-C$<em>4$H$</em>{10}$</td>
<td>0-5.66 (n=221)</td>
</tr>
<tr>
<td>n-C$<em>4$H$</em>{10}$</td>
<td>0-9.50 (n=207)</td>
</tr>
<tr>
<td>n-C$<em>5$H$</em>{12}$</td>
<td>0 – 0.9</td>
</tr>
<tr>
<td>i-C$<em>5$H$</em>{12}$</td>
<td>0-1.49 (n=112); 36.01(n=1)</td>
</tr>
<tr>
<td>Neo- C$<em>5$H$</em>{12}$</td>
<td>0-0.2 (n=24)</td>
</tr>
<tr>
<td>cyclopentane</td>
<td>0-0.024 (n=13)</td>
</tr>
<tr>
<td>n-C$<em>6$H$</em>{12}$</td>
<td>0 – 0.22 (n=18)</td>
</tr>
<tr>
<td>C$_7$-C$_9$</td>
<td>0-1.85 (n=18)</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0 – 27.63 (n=105)</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>0-2.20 (n=90)</td>
</tr>
</tbody>
</table>

Natural gas hydrates are thought to appear only in two structures – structure I, which could “take” methane, ethane and other small molecules (N$_2$, CO$_2$, H$_2$S) and structure II of the diamond package with guest molecules of methane, ethane, propane and i-butane. There is also a third structure, which was synthesized in laboratory conditions – structure H, which could invite “heavier guests” (fig. 1.3.2). Structure II and structure H hydrate are more stable than the structure I hydrate. Today, structure H is also found in nature – for example, Barkley Canyon gas hydrate contains hexane and heptane isomers$^{56}$, or gas hydrate with abnormal C$_5$ content (36.01%) was discovered in the Sea of Marmara$^{57}$. 
However, of most significant concern is the problem of climate change, which is nowadays linked to the natural gas hydrates. Global warming, which is caused by the emissions of greenhouse gases, could lead to the dissociation of hydrates, releasing the trapped hydrocarbons into the atmosphere. Various investigations of the hydrate dissociation in the Siberian Arctic shelf showed a million metric tons of hydrocarbons released into the atmosphere\textsuperscript{58,59} with the dramatic exceedance in some regions up to 100 times above average level. The process of gas hydrate melting is involved in the circular process, where the increase in the mean surface temperature leads to the increase in hydrocarbon emissions from natural gas hydrates with the ensuing transformation to CO\textsubscript{2}, leading in consequence, to a rise in the surface temperature with the warming of permafrost areas (fig.1.3.3).

\textbf{Figure 1.3.2} Various structures of gas hydrates clathrates
Nevertheless, it is still unclear (fig.1.3.4) what contribution is made by natural gas hydrates to the overall global hydrocarbon budget. It is evident that the concentration of methane emitted from natural gas hydrate is rising every year (fig.1.3.5). For example, just the land permafrost of Siberian Arctic shelf emitted 17 Tg of methane per year (2013) which is six times higher than estimated in 2006 (3.8 Tg)\textsuperscript{60-62}. 

\textbf{Figure 1.3.3.} The mechanisms of natural gas leakage through the decomposition of gas hydrates.
Figure 1.3.4 Arctic methane concentrations up to December 2018. A monthly peak of 1976.92 ppb was reached in February 2017.

Figure 1.3.5 (Sources of atmospheric methane. Present estimation. Source: U.S. Department of Energy's Methane Hydrates R&D Program

It is essential to note that if we avoid the extreme hypothesis of hydrate dissociation (more than 5% of gas hydrates could be dissoci-
ated), we can address the hypothesis of sustainability. This hypothesis is based on the assumption that it would only be possible for 3.5% of hydrate inventory (which according to ESAS is 1700 Gt) to be affected by climate change. If we only take the Siberian Arctic shelf gas hydrates (1400 Gt), we would receive 49 Gt (3.5% of 1400) of hydrocarbons, which could be released to the atmosphere. Moreover, if we decrease the per cent to 1, we will have the 14 (1% of 1400) Gt of hydrocarbons released (currently there is 5.1 Gt of methane in the atmosphere), which then will transform to approximately 38.5 Gt of CO$_2$ (see the calculations in the Appendix chapter).

1.4. Deep hydrocarbons

During recent decades deep hydrocarbons were identified in the broad spectra of geological settings, volcanic gases, hydrothermal systems, crystalline rocks and seeping processes. At present, the existence of deep hydrocarbons has been proven – there is clear experimental and theoretical evidence for the deep origin of some of the hydrocarbons present on the Earth. Deep hydrocarbons require a specific type of study based on the reproduction of high pressures and high temperatures, which are relevant for the deep interior of the Earth. Notably, all of the studies dealing with deep hydrocarbons and their high-pressure high-temperature behavior are concentrated around methane and polycyclic aromatic compounds. However, the conditions which are chosen for most high-pressure research are far from those which exist in the deep interior of the Earth. For instance, dissociation of methane was studied in the pressure range of 10-50 GPa, at a temperature of 2000-3000 K. In these studies, the chemical transformations of methane into soot, diamonds and hydrogen were reported with no signs of hydrocarbons.

In the results of the study of methane and hexane at extreme thermobaric conditions are presented. It was shown that methane melts congruently below 40 GPa. At low P–T conditions relevant for the
Earth’s upper mantle it was detected that methane is the main component of C–H fluid. At T>1200 K, heavier hydrocarbons were formed in the C–H system. In the case of hexane (C₆H₁₄) its decomposition to graphite and methane was observed at 5 GPa and 1200 K. At 40 GPa and 2000 K the unsaturated hydrocarbons were detected using Raman spectroscopy. The conditions, which were chosen for this particular investigation are focused more on the planetary interiors and cover only some of the pressure and temperature range which are relevant for our study.

One of the few comprehensive studies with the conditions corresponding to the conditions of the upper mantle is the work of Kolesnikov et al. This investigation supports the formation of ethane, propane and butane from methane in a range of pressures and temperatures compatible with upper mantle conditions, i.e., P ≃ 2–5 GPa and T ≃ 1000–1500 K. This study also reveals the chemical transformations of ethane with the formation of complex hydrocarbon systems of different composition. Above the temperature of 1500 K, both methane and ethane dissociate to soot and molecular hydrogen.

Several studies are also dedicated to the investigation of the formation of C-H systems at extreme thermobaric conditions. Using various mixtures of carbon donors (carbonates – CaCO₃ or MgCO₃) and hydrogen donors (water H₂O or Ca(OH)₂) it was possible to synthesize methane (5–11 GPa, 773–1873 K or 5–9 and 823 K), C₁-C₆ hydrocarbons (3–5 GPa, 1500 K) and heavy hydrocarbons up to C₁₆ and oxygen-derivatives of hydrocarbons (3 GPa and 1400 °C). These observations support the idea of the deep origin of hydrocarbons, showing that, besides the fact that hydrocarbons can exist and take part in various processes, they could also be formed at the particular conditions during the abiogenic synthesis from donors of carbon and donors of hydrogen.

Findings mentioned above are described in detail in the review of Kolesnikov et al.
In summary, sources of emission of hydrocarbons into the atmosphere are still unclear. The lightest saturated hydrocarbons – methane, ethane, propane and butanes play a crucial role in global carbon cycles as well as in environmental issues. Only methane and its role in atmospheric chemistry and Earth’s processes are well-studied. The most abundant hydrocarbons in the universe after methane such as ethane, propane and butanes have begun to fall within the scope of the research only very recently. Ethane, propane and butanes are widespread in the atmosphere, but their sources are poorly assessed. At the same time, recent studies have clarified that these hydrocarbons emissions account for about 20% of methane emissions. Due the oxidation process methane, ethane, propane and butane are transformed into \( \text{CO}_2 \), increasing the total amount of carbon dioxide in the atmosphere. The more hydrocarbons are released to the atmosphere; the more \( \text{CO}_2 \) can be produced due to photo-chemical oxidation.

The exponential growth of hydrocarbon content in the atmosphere may not be explained by the anthropogenic factor only. One of the dominant sources of hydrocarbon emissions deals with the gas hydrates decomposition and following release of hydrocarbons to the atmosphere. These processes were dramatically accelerated during the last decades due to the global warming. The more emissions we have, the more hydrocarbons can be released to the atmosphere and the more global warming effect can be observed.

The gas hydrates have a complex structure. A gas hydrate may consist of mixture of methane, ethane, propane and butanes located in the water cages. What is the source of the above-mentioned hydrocarbons trapped in gas hydrates? In this study it was assumed that hydrocarbons trapped in gas hydrates were formed in the Earth's deep interior. Varity in the composition of hydrocarbon systems in gas hydrates may be explained by the different thermobaric conditions of hydrocarbons synthesis (depth correspondingly) and the conditions of their upward migration. To confirm this suggestion, it is necessary to get answers two questions:

- which composition of the hydrocarbon mixture is preferable at certain thermobaric conditions?
• how can the composition of such kinds of mixtures change with a change in thermobaric parameters?

The experimental investigation of the behavior of hydrocarbon systems of different composition in the wide range of thermobaric conditions may give us answers to these questions. Before beginning this kind of investigation, it is necessary to study the transformation of those individual hydrocarbons, which have not been investigated at extreme thermobaric conditions so far – propane and butanes. The experimental investigation of propane and butanes transformations at the Earth’s deep interior conditions could solve the puzzle of hydrate formation, help to estimate possible hydrocarbon emissions from gas hydrates and understand the role of deep hydrocarbons in the global hydrocarbon budget.

1.5. The main objective, the research questions and structure of the dissertation

The main objective of this doctoral thesis is to study the role of deep hydrocarbons in the global hydrocarbon budget. This research refers to the investigation of the link between the deep hydrocarbons, which could exist in the Earth’s deep interior and the formation of natural gas hydrates, which could dissociate with the release of hydrocarbons to the atmosphere.

The thesis is designed to cover the above-mentioned objective through the following research question groups:

**Research question group 1:** selection of experimental methods. Which experimental methods are the most suitable for the planned high-pressure high temperature research? What are the main advantages, drawbacks and limitations of the different methods? Chapter 2 and all of the appended papers are focused on these research questions.

**Research question group 2:** investigation of high-pressure behavior of propane and butanes at ambient temperature. What kind of transformations happen with propane and butanes at high pressure at ambient temperature? Are they stable under these thermobaric conditions or do they transform into CO₂ or other hydrocarbons?
Chapter 3 and papers A and B are devoted to answering these research questions.

**Research question group 3:** study of the chemistry of propane, under extreme thermobaric conditions. Does propane transform into CO2 under upper mantle thermobaric conditions? Is propane stable under the extreme thermobaric conditions corresponding to the Earth’s upper mantle? Chapters 4 and papers C and D aim to answer these research questions.
Chapter 2. Methodological issues of experimental study of high-pressure hydrocarbon behaviour

The presented thesis deals with complex high pressures and high temperatures techniques including calibration, special preparation steps, experiment itself and applying various physico-chemical methods for product analysis.

All of the appended papers deal in a certain way with high-pressure methods development and improvement. Investigation of high-pressure synthesis and behavior of hydrocarbon compounds requires a special approach – starting from sample preparation and ending with a combination of novel methods of analysis with high-pressure equipment and the interpretation of obtained results.

2.1. High-pressure equipment for hydrocarbon investigation

Over recent decades, high pressure equipment has become an extremely effective tool for research of novel phenomena and of exploring new materials. With the discovery and development of high-pressure equipment by Bridgman\cite{bridgman} many studies were conducted in this field. For example, it was found that some materials undergo superconducting transition under high pressure as well as that some insulators become metallic at high pressure.

With further development of high-pressure techniques many scientists from various fields started to use high-pressure equipment for their research. Geoscientists were attracted by high-pressure tools due to the effectiveness of pressure in the study of the new phase transitions and phases of minerals, triggering the chemical reactions, conformational and structural transformations of molecules, polymerization, phase transitions, polymorphism and structure–property relations.

High-pressure science made it possible to see what could happen in the Earth’s mantle and even in the core. Moreover, this science
provided an opportunity to model the conditions of the planets of the Solar system in order to understand their formation and evolution over time\textsuperscript{87–89}. With the help of high-pressure science, the chemical composition of the layers of the Earth as well as their physical and chemical properties are being investigated.

The modeling of hydrocarbon formation in the conditions corresponding with the Earth's mantle is also a big scope of interest for geoscientists\textsuperscript{71,77,82,90}. Despite the variety of methods for creating high-pressures and high temperatures, in this study we have used diamond-anvil cells for the investigation of individual hydrocarbon high-pressure behavior.

2.1.1 Diamond-anvil cells and their application to the investigation of the hydrocarbons high-pressure behaviour

Knowledge of hydrocarbon high-pressure high temperature phase behavior is the first step towards understanding the mechanism of hydrocarbon generation in the Earth's upper mantle. Methane and ethane are the most investigated hydrocarbons. However, propane and butanes are also major constituents of all hydrocarbon phases obtained during abiogenic synthesis\textsuperscript{91,92} as well as being present in various natural systems\textsuperscript{70}. The DAC-technique was chosen due to the possibility of working with gaseous compounds in a relatively simple way (in comparison to LRV apparatuses). Another strong advantage of DAC in the investigation of the behavior of hydrocarbons is an easy access to the observation of chemical or physical processes in-situ with the usage of various methods of analysis.

DAC is a universal technique, introduced in the middle of previous century, for the research of matter under conditions of extreme pressure and temperature (figure 2.1.1). Nowadays DAC is able to generate pressures of up to 1 TPa\textsuperscript{94} which is greater than the predicted pressure of the Earth's core (~360 GPa)\textsuperscript{95}. Transparency over a broad range of radiation allows the various spectroscopic studies for DAC – from IR to γ-ray regions.
The following reagents and materials were used:
propane – 99.99 % Linde Gas Polska;
n-Butane– 99.99 % Linde Gas Polska;
i-Butane – 99.99 % Linde Gas Polska;
Re – plates 250 µm, 99.98 %, Aldrich;
steel-plates 250 µm, 99.98 %, Aldrich;
Au-foil 5 µm and Au-powder, 99.99 % Aldrich;
ruby chips ~3-5 µm, Aldrich.

Sample preparation:
After cooling the hydrocarbon (propane, normal or iso-butane) with the help of liquid nitrogen, the sample was then cryogenically loaded (more thorough description of cryogenic loading is presented in specific chapter) in symmetric BX-90-type diamond anvil cells (DAC) equipped with synthetic, CVD-type IIa diamonds with a culet size of 250 µm (figure 2.1.1). DAC was installed into a special gas loading chamber, that was flushed with liquefied hydrocarbon 3 times during pressurizing to 0.1 GPa and released.

Before the starting of rhenium gasket indentation, the gasket was cleaned with acetone in an ultrasonic bath, then it was compressed to a thickness of 35 µm, and a hole 110 µm in diameter was drilled in the center of the gasket to form a cylindrical sample chamber. The procedure of pre-indentation was also made on steel plate to ensure that the diamonds were aligned correctly.

**Figure 2.1.1** Parts of diamond anvil cells consisting of two metallic body parts named piston and cylinder (A) with mounted polished WC seats and diamonds on top of them. B – the closed DAC (with the sample).
Spectral measurement:

The Raman spectra were obtained by exciting with a He-Ne laser (632.8 nm excitation) and acquired with the help of computer software «LabRam» with a 2 cm⁻¹ spectral resolution (figure 2.1.2). To measure the pressure in the cell, a ruby chip of approximately 5-7 µm in diameter was put into the pressure chambers near the center of the hole (between the edge and the center), and the change in the pressure was determined using the shift in the ruby luminescence line.

Figure 2.1.2 The scheme of Raman spectrometer.

Despite many similarities between the application procedures of IR and Raman spectroscopy in the investigation of hydrocarbon systems, in the case of propane it was decided to use the combination of these two methods. Lately, for the normal and isomeric butane studies, only Raman spectroscopic study was performed. The IR
spectra were collected 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 cm$^{-1}$. Ruby chips approximately 5 µm in size were placed in the samples for the pressure determinations. The spectra obtained were analyzed using OPUS v7.2.139.1294 software. The uncertainties in the Raman and IR peak positions were ±1 cm$^{-1}$ in both methods.

The pressure in the cell was measured before and after the collection of Raman or IR spectra due to the necessity of determination of the hysteresis value. In our experiments, the hysteresis value does not exceed the error in the pressure measurement using the ruby luminescence line (±0.5 GPa). Another important note is that Raman and IR spectra were collected both for compression and decompression experiments to reveal the differences in hydrocarbons phase behavior.

Pressure determination includes measurement of the ruby fluorescence radiation wavelength position and comparison with known shift of pressure-dependent shift to longer wavelength of the R1 and R2 ruby emission lines.

The characteristics of these lines are the following (figure 2.1.3):

1) narrowness;
2) high quantum yield;
3) strong pressure dependence shift.

The resolution of the R1 and R2 lines is an indication of the quasi-hydrostatic character of the environment. The linear calibration of the ruby fluorescence emission is reliable up to 30 GPa for a quasi-hydrostatic environment.
Figure 2.1.3. Ruby fluorescence spectrum at 7.7 GPa (upper). The empirical dependence of R1 line shift with pressure.

The precision of the pressure measurements by ruby techniques is ±0.5% above 20 GPa under hydrostatic conditions. The empirical equation which shows the connection between the pressure and the ruby wavelength is:

\[
P = \frac{A}{B} \left[ \left( \frac{\Delta \lambda}{\lambda_0} + 1 \right)^B - 1 \right]
\]  

(2.1.1)
where $P$ – pressure (GPa), $A$ and $B$ – empirical constants. $\lambda_0$ – the wavelength (nm) of the R1 ruby fluorescence line at the ambient conditions, usually the room one. $\Delta \lambda = \lambda - \lambda_0$ - the R1 signal shift with pressure.

### 2.1.2 Laser-heating in DAC

To generate high temperatures in DACs two methods could be applied – external electrical resistive heating and laser heating. While performing the investigations for the current thesis, we used the double-sided laser heating technique, which covers a higher temperature range (800-6000 K). The double-sided heating makes it possible to avoid large thermal gradients (if we compare it with one-sided laser heating).

To measure the temperature in this type of the experiment, collection of the thermal radiation of the heated sample and its fitting with the Planck equation for the black-body emission were carried out:

$$I(\lambda) = \frac{\varepsilon c_1 \lambda^{-5}}{e^{c_2 / \lambda T} - 1} \quad (2.1.2.1)$$

where $I(\lambda)$ is the measured intensity, $\varepsilon$ is the emissivity, and $c_1 = 3.67 \cdot 10^{19}$ and $c_2 = 1.4388 \cdot 10^7$, $T = 2684$ K. Emissivity is taken as 1, but it is in fact corrected by the fitting of empirical parameters, namely $c_1$.

The laser heating of propane was performed at the laser heating setup at the Bayreuth Geoinstitut. Heating of the sample was provided by two YAG (yttrium-aluminum-garnet) lasers (1064 nm central wavelength). For temperature measurements the thermal emission spectra of the heated area was guided into an IsoPlane SCT 320 spectrometer with a 1024x256 PI-MAX 4 camera. Temperature was determined by fitting of the black body radiation spectra of the heated area in a given wavelength range (570-830 nm) to the Plank...
radiation function. Liquid or solid propane is optically transparent and does not absorb well at the central wavelength of the YAG laser, which means that it is important to find a way to heat the sample and, moreover, eliminate the catalytic influence of the absorber (which could appear in terms of the usage of noble metals such as Ir or Re). For these reasons, gold foil was employed in the role of absorber of the laser radiation to dissipate heat to the sample (figure 2.1.2.1). The Raman spectra were collected in the hot point, cold sample areas and in the few points of the transition zones.

![Figure 2.1.2.1.](image)

**Figure 2.1.2.1.** The DAC sample chamber with the method of collecting Raman spectra after laser-heating technique.

Collection of the Raman spectra was carried out in the hot point as well as in the cold sample areas in order to gain deeper understanding of the hydrocarbon behavior while it is affected by the extreme temperatures.
2.1.3 Cryogenic gas loading

Gas-loading system with the compactness and easiness in operation was designed and constructed specially for this study. The built system is safe, user friendly, and flexible, which means that it could be modified and updated for the particular need. The process of cryogenic loading is a well-known technique showing its effectiveness for liquefaction of gases, which have their boiling temperature higher than the boiling temperature of liquid nitrogen. Non-methane hydrocarbons were easily able to be loaded into the DAC. The procedure of gas loading was carried out via the following steps: the diamond-anvil cell equipped with the rhenium (in our case) gasket was installed in the special loading chamber which itself was placed in a Styrofoam container. After that, this container was filled in with liquid nitrogen. Hydrocarbon (propane or butanes) from a gas bottle was then directed to the loading chamber, where the processes of cooling and liquefaction were started. With the opening of the loading chamber, the DAC must be closed for the purpose of trapping the particular amount of gas by tightening the screws. The need for a balloon in the system could be explained as follows. The pressure in the closed chamber needs to be supported during the process of liquefaction. Another important feature of the balloon is that it isolates the chamber from the atmosphere and protects from the injection of unnecessary compounds in the system (such as droplets of liquid nitrogen).

The schematic representation and the photographs of the cryogenic loading system are shown in figure 2.1.3.1.
Figure 2.1.3.1. The schematic representations of the cryogenic loading unit (a) with photographs of its exact view – the whole unit (b) and the sample chamber in the Styrofoam container (c).
2.2 Raman and IR spectroscopy and their applications to hydrocarbon investigation

Vibrational spectroscopy is a non-destructive, non-invasive energy sensitive method that may be applied for identification, characterization, structure elucidation, reaction monitoring, quality control, and quality assurance\textsuperscript{100,101}. The specific types of vibrational spectroscopy are Infrared (IR) and Raman (combinational scattering) spectroscopy. These techniques measure changes in the vibrational state of molecules.

The Raman shifts, i.e. bands in a Raman spectrum reflect the interaction of the incident light with a particular vibration of the nuclei. The vibrations of the nuclei depend on their sizes and masses, valences, and the forces between atoms, and the symmetry of a crystal structure. These factors affect the number of Raman bands, their relative intensities, their widths and polarizations. Raman spectra can be obtained in situ in DACs as diamonds are transparent in this region of electromagnetic radiation. Changes in Raman spectra at various pressures mean that the sample undergoes structural change – phase transition.

Raman spectroscopy proved its place as an extremely useful tool for rapid analysis of vibrational, electronic and magnetic systems, providing extreme versatility of the obtained results. Being one of the most informative methods for studying the material properties under extreme conditions of high pressure, Raman spectroscopy is a perfect method for investigation of phase diagrams, superconductors, magnetic compounds, chemical reactivity of simple molecules and so forth.

Raman spectroscopy also successful for the investigation of hydrocarbon systems, from both qualitative and quantitative perspectives, making it one of the most relevant methods in petroleum chemistry\textsuperscript{102,103}.

Recently, Raman spectroscopy also proved its efficiency in the high-pressure study of hydrocarbon compounds and products of their interactions. However, despite widespread application of Raman spectroscopy to high-pressure science, its implications for high-pressure investigation of hydrocarbon compounds are limited...
and it requires a comprehensive review, which is presented below.

Hydrocarbons are a diverse class of organic compounds, which consists of alkanes, alkenes, alkynes and aromatics. Knowledge of their high-pressure behavior is beneficial for different purposes, especially with the note that hydrocarbons occur on Earth and in the Solar System in various thermodynamic conditions. In this thesis, the hydrocarbons were mainly analyzed qualitatively. The main and the most striking feature of Raman spectroscopy is the ability to provide a great wealth of easily analyzable information very rapidly. Unfortunately, Raman spectroscopy is not a «cure to all diseases» and its usage in the experiments could be limited, especially when the mixtures of compounds of the same nature exist. This means, that for analysis of crude oils or other complex hydrocarbon mixtures Raman spectroscopy could answer the following types of question: “Are there any bands of aromatic compounds on the spectra?” or “Do we have in the products’ mixture only normal alkanes or could we also see alkanes of branched structure?”. In Raman spectra of hydrocarbons, very clear and sharp spectral differences among the components were able to be observed. Most useful information is located at the 3200–2500 cm\(^{-1}\) and 1700–300 cm\(^{-1}\) regions (Table 2.2.1, based on 107–112). In the case of 5-10 compounds in the mixtures, it is still possible to decode the spectra and obtain the signatures of the individual compounds, which were able to be found in the region of “fingerprints” (300-1700 cm\(^{-1}\)). The Raman bands of heavy hydrocarbons are usually weaker than those of the lighter ones. However, they are more robust due to the character of the spectra in the spectral range corresponding to the skeleton C-C vibrations, which are always individual for hydrocarbons with different carbon compositions, intramolecular bonding or molecular geometry (cyclic or chain-like). Moreover, this identification is confirmed by observations of the C-H deformation modes, which differ for the saturated hydrocarbons of different chain length.
Table 2.2.1. Raman characteristics of 4 main hydrocarbon groups of petroleum systems

<table>
<thead>
<tr>
<th>Hydrocarbon group</th>
<th>Basic Raman signatures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal (linear) alkanes (paraffins)</td>
<td>The hydrocarbon homologues (i.e. hexane, heptane, octane) have nearly the same Raman spectrogram. Very strong spectrum peaks at 2700 - 2970 cm(^{-1}). The methyl (CH(_3)) Raman peak (2872 cm(^{-1})) is the strongest at normal paraffin; The rocking and wagging modes of CH(_2) groups - 720-760 cm(^{-1}) and 1300-1340 cm(^{-1}); CH(_2) deformation frequencies 1440-1470 cm(^{-1}) (bending/scissoring); CH(_2) twisting 1100-1350 cm(^{-1}); Strong peaks in the region of 800-1000 cm(^{-1}) (C-C stretching of n-alkanes) are common for all alkanes, i.e.: n-butane – 837 cm(^{-1}); n-pentane – 869 cm(^{-1}); n-hexane – 898 cm(^{-1}); n-hexadecane – 888 cm(^{-1}); C-C skeletal stretching vibrations are a function of chain length.</td>
</tr>
<tr>
<td>Branched (isomeric) alkanes (paraffins)</td>
<td>The methylene (CH(_2)) Raman peak (2911 cm(^{-1})) is the strongest at isoparaffin; The particular peak of branched methyl is 748 cm(^{-1}); Single branching of the hydrocarbons gives rise to characteristic frequencies of C-C stretching vibrations in the regions 1180-1140 cm(^{-1}) and 830-790 cm(^{-1}); double branching gives similar frequencies in the regions 1260-1190 cm(^{-1}) and 760-710 cm(^{-1}); More than two methyl groups give rise to the characteristic frequencies in the regions 970-950 cm(^{-1}) and 930-910 cm(^{-1});</td>
</tr>
</tbody>
</table>
The deformational modes of CH groups - 1330-1360 cm\(^{-1}\);
Additional strong peaks due to the particular configuration of carbon atoms:
Tert-butyl 680-750 cm\(^{-1}\)
Isopropyl 740-830 cm\(^{-1}\)
Internal quaternary carbon atom 670-710 cm\(^{-1}\)
Internal tertiary carbon atom 800-860 cm\(^{-1}\)
Two adjacent tertiary carbon atom 730-760 cm\(^{-1}\)

| Cycloalkanes (naphthenes) | The methylene Raman peak (2857 cm\(^{-1}\) ±) is the strongest at cycloparaffin. The position of the ring breathing peak can change slightly as a function of substituted groups, strong peaks in the 700 cm\(^{-1}\) to 1000 cm\(^{-1}\) range can signify the presence of cycloalkanes (i.e. cyclopentane 886 cm\(^{-1}\), cyclohexane 802 cm\(^{-1}\), cyclobutane 1002 cm\(^{-1}\)) methylene-scissoring ~1450-1460 cm\(^{-1}\) (i.e. cyclopentant 1455 cm\(^{-1}\), cyclohexane ~ 1452 cm\(^{-1}\)) |
| Aromatic hydrocarbons (arenes) | Two Raman spectrum characteristic peaks of phenyl (breathing vibration of benzene ring 988 cm\(^{-1}\)±, C-H symmetric stretching 3058 cm\(^{-1}\)± ); Weaker ring vibration is observed at 610 cm\(^{-1}\) Sharp C-H bands attached to the benzene ring, which are noticeably different from aliphatic C-H bands, are clearly observed at 3050 and 1650 cm\(^{-1}\); Because aromatic hydrocarbons have strong fluorescence, there is one (3000 cm\(^{-1}\)±) or two (2000 cm\(^{-1}\)± and 3000 cm\(^{-1}\)±) fluorescence wide peaks at their Raman spectrograms; |

Note: in this Table only the information about natural constituents of petroleum systems is presented. The hydrocarbon groups of alkenes and alkynes could only be obtained during the chemical reactions of natural hydrocarbons and rarely presented in the crude oils or natural gases.
Chapter 3. High-pressure behavior of propane and butanes at ambient temperature

One of the main directions of the present study (see paragraph 1.4. Objectives) was the determination of the limit parameters of the deep formation of hydrocarbons.

The starting point of every high-pressure investigation is the collection of data on the behavior of compounds at values of extreme pressure without temperature influence. It is common knowledge that, for example, ethylene and propylene react under high pressure at ambient temperatures\textsuperscript{113,114} producing long-chained hydrocarbons with various structure. Before the high-pressure high temperature study is conducted, it is necessary to understand the influence of the pressure factor on the molecule. Individual hydrocarbon compounds were explored mainly using the DAC technique combined with vibrational spectroscopy\textsuperscript{115,116}, but also other methods were implemented for this purpose, especially XRD\textsuperscript{117}, shock-compressions experiments\textsuperscript{118} and computational studies\textsuperscript{119}. The DAC technique allows ultrahigh pressures to be generated. It is the easiest and safest method among high-pressure techniques, while vibrational spectroscopic methods are able to provide easy-to-analyze data without any destruction of the initial compound. The results of the investigation of propane and two isomeric butanes are presented in this chapter. The investigation was conducted using DACs with type IIa diamonds and Raman spectroscopy as a main method for analysis of pressure influence on molecular structure. Despite the fact that hydrocarbons such as methane and ethane with higher homologues like pentane, hexane and even higher were analyzed thoroughly by Raman or IR spectroscopies\textsuperscript{115,120-124}, propane and butanes are the missing “puzzle” in the chain of investigation of saturated hydrocarbons at high-pressure.
High-pressure behavior of propane and butanes also must be known due to various problems arising in the planetary sciences\textsuperscript{125-128}, petrochemical processes\textsuperscript{129,130} and high-pressure chemistry syntheses\textsuperscript{67,131}.

Propane and n-butane and their phases in the high-pressure region were previously investigated in only one DAC/XRD-study\textsuperscript{124}, which showed that C\textsubscript{3}H\textsubscript{8} undergoes a phase transition at 3.2 GPa, while normal C\textsubscript{4}H\textsubscript{10} freezes at 1.6 GPa in the form of polycrystalline mass. However, due to another interest of this study, these hydrocarbons were only pressurized up to 6 GPa. The second isomer of butane, isobutane, was never studied by means of high-pressure techniques. Limited knowledge of C\textsubscript{3}-C\textsubscript{4} high-pressure transformations under the wide thermodynamic conditions in which these hydrocarbons could exist in the universe requires further investigation in terms of the main aims of the thesis.

The cryogenic loading of hydrocarbons, DAC and Raman/IR experimental techniques are described in detail in the second chapter of this thesis.

A change in experimental conditions (pressure, temperature, concentration of reagents or particle size) could lead to the phase transition with the following formation of new phase. To identify the phase transition or new phase, the vibrational mode (or modes) needs to change its character on the spectra in one of the known ways:

1) it can become more (split) or less (merge) complex, for instance, by turning from singlet to triplet;
2) the modes could appear or disappear with the formation of new phase;
3) the intensity or intensity ratio of the vibrational modes could be changed substantially;
4) the formation of new compounds with the diverse vibrational modes due to the running of chemical reaction.

Raman spectra of all of the hydrocarbons could be divided in two parts - 3200-2800 cm\textsuperscript{-1} (valence vibrations) and 1700-300 cm\textsuperscript{-1} (fingerprint zone, deformational vibrations) regions.
nately, Raman spectra of alkanes presumably have the same representation due to the methyl (\(-\text{CH}_3\)) and methylene (\(-\text{CH}_2\)) bands. In spite of this, all of the alkanes have their own characteristic modes, which could help to distinguish one hydrocarbon from another and which are located in the "fingerprint zone".

The propane molecule is one of the simplest hydrocarbons (the third member of the alkane homological series). At the same time, its vibrational properties are complex, as it possesses 27 distinct vibrational modes at ambient pressure and temperature.

In this part of the study, the pressure dependence of propane Raman shifts and wavenumbers was investigated in the region of 5-40 GPa during the compression experiments (down to 3 GPa during the decompression experiments). The complete set of the experiments with explicit descriptions is presented in Paper A, while the figures 3.1 and 3.2 plus Table 3.1 reflect the basic findings during this part of the research.
Figure 3.1. Raman spectra of C₃H₈ of collected at ambient temperature and in the pressure range 5.1 (5) – 40 (5) GPa. For clarity, the spectra were divided into three regions: (a) 800-1300 cm⁻¹, (b) 1350-1550 cm⁻¹, and (c) 2900-3100 cm⁻¹. The 1250-1350 cm⁻¹ and 2100-2700 cm⁻¹ regions are dominated by the diamond first and second-order peaks and are not shown. The hysteresis value does not exceed the error in the pressure measurement using the ruby luminescence line (±0.5 GPa).
**Figure 3.2.** IR spectra of C\textsubscript{3}H\textsubscript{8} collected at ambient temperature and in the pressure range 3.0 (5) – 42.0 (5) GPa. The spectra were divided into three regions: (a) 700-1100 cm\textsuperscript{-1}, (b) 1350-1550 cm\textsuperscript{-1}, and (c) 2800-3200 cm\textsuperscript{-1}. Because the diamond anvils are type IIa stones (nitrogen-free diamonds) whose IR absorption bands are in the range 1800-2650 cm\textsuperscript{-1} (two-phonon spectrum of the diamond), we did not consider this region. The hysteresis value does not exceed the error in the pressure measurement using the ruby luminescence line (±0.5 GPa).
Table 3.1. Phase transitions of propane observed during this investigation by means of Raman and Infrared spectroscopy

<table>
<thead>
<tr>
<th>Phase transition</th>
<th>Spectral indications</th>
<th>Raman spectra</th>
<th>Infrared spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>I - 6.4 (5)/7.0 (5) GPa</td>
<td>Particularly all of the vibrational modes became distinct in all three regions of the spectra. Increase in the intensities for all of the main vibrational modes.</td>
<td>Clear distinction of the CH$_3$ deformational modes in the region of 1400-1450 cm$^{-1}$ and the CH$_2$/CH$_3$ stretching modes (both symmetric and asymmetric) in the region of the valence vibrations. The low-intensity bands of the IR modes became sharper at the phase transition.</td>
<td></td>
</tr>
<tr>
<td>II - 14.5(5)/14.0(5) GPa</td>
<td>The further split of the doublet at ~860 cm$^{-1}$ (v$_8$ C-C skeletal stretching) to triplet with the loss of intensity for all of the other vibrational modes.</td>
<td>Merging of the C-C stretching doublet at ~930 cm$^{-1}$.</td>
<td></td>
</tr>
<tr>
<td>III - 26.5(5)/27.0(5) GPa</td>
<td>Substantial change in the intensities in the CH$_3$ deformational mode region (~1400-1450 cm$^{-1}$)</td>
<td>CH$_3$ deformational mode splitting into a doublet (~1500 cm$^{-1}$) with the ensuing appearance of distinct modes at higher pressures in this region.</td>
<td></td>
</tr>
</tbody>
</table>
As for the butane isomers, the complexity of the spectra of both n-butane and i-butane increases in comparison with propane, which is obvious due to the growing of the hydrocarbon chain. Despite the similar molecular formulae C₄H₁₀, the two isomers of butane have totally different chemical and physical properties, which affects further differences between occurrence on the Earth and application in the industry. The high-pressure behavior of butanes is also open to question following the only piece of research that examined its fate (only of n-butane) in the high-pressure region, showing its phase transition from liquid to solid at 1.6 GPa by means of XRD. Raman spectroscopy has never been used for the high-pressure investigation of n- and i-butanes. However, a small amount of research on Raman vibrational bands of both molecules was conducted in the middle of last century.

A high-pressure study of butane isomers at ambient temperature was presented in Paper B. Raman spectra, collected during this part of the research for normal butane and iso-butane are shown in figures 3.3 and 3.4.

Raman spectra of normal alkanes and iso-alkanes have a strong difference because of the branched character of the latter, which is reflected in the character of the vibrational bands. The second difference, which was noticed during the analysis of the spectra, is the presence of the rotational isomerism in the case of normal butane. N-butane is the simplest hydrocarbon, which has this property, introducing a possibility of its carbon skeleton for the rotation around its C-C bonds. This effect was also never studied at the high-pressure conditions, despite the fact that the rotational isomerism of organic molecules was extensively studied by Raman spectroscopy under ambient conditions.

Having three conformers with different C-C-C-C torsion angle, butane demonstrates a complicated vibrational behavior due to the presence of all gauche and trans conformers' bands on its spectra. Figure 3.3 shows this tendency, which could give us the understanding that no single butane conformation could fit the spectra perfectly.
Iso-butane shows totally different spectra compared to normal butane. Iso-butane is a symmetrical molecule, which means that all of the CH$_3$ groups in it are equal to each other and do not have any differences. Degeneration of iso-butane’s several vibrations and absence of conformational isomerism are leading to the simplification of the spectra in comparison to n-butane. For instance, in the region of C-H stretching vibrations (2800-3300 cm$^{-1}$) or in the region of fingerprints the –CH$_3$ fragment domination led to the higher intensities and more branched character of bands. Tertiary wagging of iso-butane ($v_{15}$) is a unique band which makes its spectra distinguishable from other hydrocarbons.

Figure 3.3. Raman spectra of n-butane collected at ambient temperature and at high pressures upon compression in the range of 1.4(5) - 40.2(5) GPa. The spectra have been divided into three regions: (a) 300-1300 cm$^{-1}$ (C-C stretching and methyl rocking region), (b) 1400-1600 cm$^{-1}$ (methyl bending region), and (c) 2800-3300 cm$^{-1}$ (C-H stretching region). The 1250-1350 cm$^{-1}$ and 2100-2700 cm$^{-1}$ regions are dominated by diamond first-second-order peaks and have not been shown. The characteristic vibrations of gauche-butane have totally disappeared from the 3.6(5) GPa, which can definitely be attributed to the phase transition and total solidification of n-butane. Between 1.9(5) and 2.4(5) a noticeable change of spectrum appearance could be seen, especially in the 2800-3300 cm$^{-1}$
diapason, (C-H stretching vibrations). This phase transition also corresponds well with the work of Podsiadlo\textsuperscript{124}, where the XRD technique was used to find the phase transition at 1.8 GPa. Another phase transition was noticed in the region between 2.4(5) and 2.9(5) GPa, with the double splitting of $v_{111}$ band, substantial rise of $v_{10}$ and $v_{9}$ intensities, the disappearance of $v_{14g}$ and $v_{32g}$ modes and the distinction of CH$_3$-bending region bands.

**Figure 3.4.** Raman spectra of i-butane collected at ambient temperature and at high pressures upon compression in the range of 1.6(5) - 37.6(5) GPa. The spectra have been divided into three regions: (a) 300-1300 cm$^{-1}$ (C-C stretching and methyl rocking region), (b) 1400-1600 cm$^{-1}$ (methyl bending region), and (c) 2800-3300 cm$^{-1}$ (C-H stretching region). The 1250-1350 cm$^{-1}$ and 2100-2700 cm$^{-1}$ regions are dominated by diamond first-second-order peaks and are not shown. As can be seen from the spectra— at pressures between 1.6(5) and 2.7(5) GPa the C-H stretching vibrations became less sharp, which is the same for the region of CH$_3$-bending. Second phase transition was noted in the interval from 2.7(5) to 3.5(5) GPa with the dramatic change of the spectrum— CH$_3$-bending vibrations became sharper and more distinct, CH$_3$-rocking vibrations $v_{6}$/$v_{16}$ transformed from triplet to doublet. With further compression of the i-butane no substantial changes were seen.
The investigation of propane and butanes in the high-pressure region at the ambient temperature revealed several principles:

1) no chemical changes were found while compressing both \( \text{C}_3\text{H}_8 \) and \( \text{C}_4\text{H}_{10} \) molecules at pressures up to 40 GPa;

2) the Raman or IR bands are consequently shifting to higher frequencies with the pressure increase mainly due to the effect of C-C and C-H bonds length and atomic distances reduction;

3) there is no correlation between the number of phase transitions and the molecular weight at pressures up to approximately 40 GPa (for butanes – 2, for propane – 3, for methane – 5);

4) the structure of the molecule doesn’t affect the number and the character of phase transitions in the case of butane isomers;

5) nearly 70% of different vibrations or their merged versions are presented on the spectra in a whole range of pressures;

6) the above-mentioned observations have opened the ground for the high-pressure high temperature studies, mainly the study of propane, which is described below. These results were presented in Papers C and D.
Chapter 4. High-pressure high temperature behavior of propane

The role of propane and other hydrocarbons in the global carbon cycle, especially in its geological part, is clearly of interest and was poorly investigated. Our knowledge of propane high-pressure behavior is very limited, especially at extreme thermobaric conditions. It is known that high-pressure conditions could substantially change atomic or molecular interactions in the condensed matter. Another issue is that when we combine high pressure with high temperatures the possibility of discovering new phases and overcoming kinetic barriers rises. The temperature studies of propane are common and extensively highlighted during the petroleum era primarily due to the development of petrochemical processes such as catalytic/thermal cracking or pyrolysis\textsuperscript{136-140}. Pyrolysis and cracking are processes which are operate at elevated temperatures with the purpose of decomposing the initial molecules to low-molecular weight compounds. In the case of propane, the decomposition is to ethylene and propylene, which are then used for petrochemical needs.

Propane, as a widely applied petrochemical feedstock and a major component of LPG, was the subject of much effort regarding the study of its chemical reactivity under the high temperatures of the pyrolysis process. High temperature cracking of propane, as with every cracking of hydrocarbon species, may produce hundreds of compounds and then open up many reaction pathways\textsuperscript{139}. The products mixture of propane pyrolysis could vary and the final yield depends on temperature, pressure, feedstock, residence time, type of the reactor and catalysts\textsuperscript{139,140}. The most commercial and well-known version of the pyrolysis of propane is always using a 550-900 °C temperature range\textsuperscript{139,140}. This process is always divided into two stages. The first stage deals with the decomposition of propane through a free-radical chain mechanism with the formation of methane, ethylene, propylene and hydrogen\textsuperscript{141}. The second stage encompasses more complicated reactions, which involve produced compounds into secondary reactions, mainly olefins. Here, the polymerization and polycondensation reactions play a major role
and lead to large stable structures like aromatic compounds, dienes, cyclophanes\textsuperscript{139}. Then the formation of solid products starts with the formation of related to each other polycyclic aromatics (tar) and gaseous carbon\textsuperscript{139,142} originated, probably, due to acetylene for-
mation \textsuperscript{140}. The pressure aspect of this process has never been ques-
tioned, for one reason – high pressure causes the unwanted secondary reactions to prevail, leading to the formation of tar rather than of gases like ethylene and propylene\textsuperscript{139}.

Methane and ethane came within the scope of such research on several occasions, mostly, due to their prevalence in nature and greater interest for research\textsuperscript{73,143-148}. Different research groups propose various mechanisms of hydrocarbon HPHT transformations, making the problem of hydrocarbon fate in the Earth’s deep interior mainly unsolved. Contradictions within existing results prepare the ground for this study and pose a question regarding the real role of propane in the mantle processes and the formation of further natural gas hydrates.

Knowledge of propane HPHT transformations is necessary not only for geosciences, but may also be relevant for planetary systems processes, both in the atmosphere\textsuperscript{149} and the interior of the space objects\textsuperscript{150}. Deeper understanding of propane’s role at certain thermobaric conditions is also interesting for diamond synthesis or other related HPHT synthesis\textsuperscript{151}.

Propane was loaded using the same technique as in the non-tem-
perature experiments with only one exception – a thin gold foil \textasciitilde1 µm was employed in the cell for propane heating. The main function of the gold foil was to effectively absorb the laser energy and, therefore, heat the sample. Propane, like many light hydrocarbons is transparent to the laser’s wavelength, which requires a specific approach to its heating via metal foils, which play the role of internal furnace. A detailed description of the procedure is described in chapter 2. The Raman spectra were collected at 3,6,8,11,14,17 and 22 GPa in the temperature range \textasciitilde800-2500 K and presented in figures 3.5-3.8.

The spectra of the transformations of propane at 8, 17 and 22 GPa are described thoroughly in papers C and D.
Despite the fact that all of the spectra registered during the current investigation look different, they have similar trends – the presence of carbon bands and C-H and/or C-C vibrations. This observation highlights a two-direction mechanism of propane transformations. Propane could decompose with the formation of low-molecular compounds and it could be involved in the polymerization and polycondensation reactions, which spiral into the broad range of long-chained, cyclic and aromatic hydrocarbons. The products obtained suggest that high-pressure high temperature reactions of propane have a lot in common with the classic chain mechanism of hydrocarbon pyrolysis or cracking. The main similarity of all of the obtained spectra is stability of propane up to 900 K, which means that this compound remains mainly untouched in a broad range of temperatures. This regularity is also in a good correspondence with the previous work of Kolesnikov et. al. 77, where the stability of methane and ethane has been shown at temperatures <1000K.

**Hydrocarbon formation**

During the analysis of Raman spectra, it was observed that at every pressure point hydrocarbon formation from initial propane was registered. For example, the formation of n-alkanes of C₁-C₆ (from methane to n-hexane) structures at pressures of 11 and 14 GPa via a well-known chemical mechanism where propane decomposes to methyl, ethyl or propyl radicals, which further react with other molecules or free radicals or even recombine (3.1.):

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_3 & \xrightarrow{\text{reaction}} \text{CH}_3\text{CH}_2 + \text{CH}_3 \\
\text{CH}_3\text{CH}_2\text{CH}_3 + \cdot \text{CH}_3 & \xrightarrow{\text{reaction}} \text{CH}_4 + \text{CH}_3\text{CH}_2\text{CH}_2 \\
\text{CH}_3\text{CH}_2\text{CH}_2 + \cdot \text{CH}_3 & \xrightarrow{\text{reaction}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \\
\text{CH}_3\text{CH}_2 + \text{CH}_3\text{CH}_2\text{CH}_3 & \xrightarrow{\text{reaction}} \text{CH}_3\text{CH}_3 + \text{CH}_3\text{CH}_2\text{CH}_2 \\
\text{CH}_3\text{CH}_2 + \text{CH}_3\text{CH}_2\text{CH}_2 & \xrightarrow{\text{reaction}} \text{CH}_3\text{CH}_3 + \text{CH}_3\text{CH}_2\text{CH}_2
\end{align*}
\] (3.1.)
The appearance of the first six members of the n-alkane homologous series at 11 and 14 GPa and T>900 K is in good agreement with earlier results by Kolesnikov et. al. and computer simulation experiments by. It is important to note, that the formation of isoalkanes was not registered on all of the spectra. However, we assume that the bands of all of the hydrocarbon groups could merge making identification nearly impossible. However, the presence of n-pentane and n-hexane had never been reported previously. This means that smaller n-alkanes could be polymerized to the higher ones. The difference between the current two spectra (at 11 and 14 GPa) lies in the presence of hydrogen in the case of 14 GPa spectrum, which could be explained by the hydrogen high diffusion processes or by the involvement of a hydrogen molecule in the secondary reactions. The polymerization mechanism seems suitable for such cases as does the mechanism of Fischer-Tropsch synthesis due to the certain regularity between the intensity of vibrational bands and the molecular weight (3.2.):

\[
\begin{align*}
\text{Propylene or ethylene or other unsaturated hydrocarbons could be generated easily in the reactions of pyrolysis due to the dehydrogenation reactions or possibly due to the chain radical reactions of cracking (3.3. and 3.4.)}:\\
\text{C}_3\text{H}_8 &= \text{C}_3\text{H}_6 + \text{H}_2 \\
\text{C}_2\text{H}_6 &= \text{C}_2\text{H}_4 + \text{H}_2
\end{align*}
\]
The resulting reaction of hydrocarbon synthesis could be modified from\textsuperscript{77}:

\[ \text{CH}_4 \rightarrow \text{C}_2\text{H}_6 + \text{C}_3\text{H}_8 + \text{C}_4\text{H}_{10} + \text{C}_5\text{H}_{12} + \text{C}_6\text{H}_{14} \ldots + \text{H}_2 \]

The obtained spectra also show us the \textit{contemporaneous presence} of hydrocarbons, hydrogen and graphite which means equilibrium occurs in the cell.

\textit{Carbon and complex hydrocarbon systems formation}

The main chemical transformation of propane at 3 and 6 GPa (figures 3.7 and 3.8) is a chemical reaction with the prevailing generation of carbon, which has Raman spectra very similar to the common black solid compound called soot. Soot is always produced during all petrochemical processes which involve high temperatures - mainly pyrolysis, catalytic cracking, reforming and other. Soot and
coke are common by-products of petroleum refining and petrochemistry and are always regarded as an unnecessary participant of the processes due to their strong action as a catalytic poison\(^1\) (3.5.):

\[
\begin{align*}
C_3H_8 &= 3C + 4H_2 \\
C_xH_y &= xC + (y/2)H_2
\end{align*}
\tag{3.5.}
\]

Another type of carbon which may occur in such types of reaction, is graphite. During high-pressure high temperature processes graphite may be generated in two forms – highly ordered and disordered. But according to\(^1\), in our case we are dealing with disordered phases of graphite or even sooty material. Highly-ordered graphite possesses only one Raman band at 1580 cm\(^{-1}\) on the spectra (so called G-band), on the contrary, disordered graphite provides the spectra also with D-bands at 1360 and 1620 cm\(^{-1}\) in terms of ambient pressures and temperatures\(^2\). Raman bands of soot and graphite are hard to distinguish from each other, but according to the literature sources, soot has broader peaks\(^1,2\).

We did not find any signs of hydrogen in the Raman spectra of propane chemical transformations at 3 and 6 GPa. Usually, the hydrogen vibrational modes occur in the region of 500-900 cm\(^{-1}\). The absence of hydrogen in the spectra can be explained by a high hydrogen diffusional process through the rhenium gasket of DAC.

C-H vibrations of hydrocarbons were also detected on the spectra at both 3 and 6 GPa in the region of 3000 cm\(^{-1}\). We did not identify the particular compounds due to the presence of only C-H bands on the spectra, which indicates the complex nature of the reaction products\(^3,4\). Another explanation for such an intense vibrational mode there is the prevalence of methane in the reaction cell through the following reaction, which also explains the absence of hydrogen (3.6.):

\[
C_3H_8 + 2H_2 = 3CH_4
\tag{3.6.}
\]
Figure 3.5. Raman spectra of raw propane and its products after heating and pressurizing at 11 GPa and $T = 840-2420$ K ($\pm 100$ K). The reference peaks for C-H valence of saturated hydrocarbon compounds were taken from $^{137-139, 146}$, for unsaturated – from $^{146, 147}$, for graphite (soot) modes were taken from $^{154, 155}$. The reference peaks for C-C stretching and C-C bending of hydrocarbons were taken for ethane from $^{77}$, for propane from $^{77}$, for n-butane from $^{77, 156}$, for n-pentane $^{157}$, for n-hexane $^{158}$. The propane remained stable at 840 K and below. The spectra of untouched propane correspond well with the previous experiments carried out by me and my research group $^{159}$. 
Figure 3.6. Raman spectra of raw propane and its products after heating and pressurizing at 14 GPa and T = 930-1580 K (±100 K). The reference peaks for C-H valence of saturated hydrocarbon compounds were taken from 137-139, 146, for unsaturated – from 146,147, for graphite (soot) modes were taken from154,155. The reference peaks for C-C stretching and C-C bending of hydrocarbons were taken for ethane from77, for propane from77, for n-butane from77,156, for n-pentane157, for n-hexane158. The propane remained stable at 930 K and below. The spectra of untouched propane correspond well with the previous experiments carried out by me and my research group140.

The phase behavior of propane while increasing the pressure changes dramatically. Moreover, the appearance of unsaturated hydrocarbons on the spectra in the range between ~3100-3200 cm\(^{-1}\) could be seen. Saturated hydrocarbons were also formed under these conditions (~3000 cm\(^{-1}\)). The strong fluorescence in the C-C stretching region prevents identification of the individual hydrocarbons. Such compounds are formed mainly during the reactions of polymerization, polycondensation or aromatization, for example, via allyl-radical chain mechanism (3.7):
Unfortunately, the spectroscopic methods do not give us the possibility to answer the question about the nature of such a complex mixture of compounds. But there is evidence that such mixtures consist of high-molecular hydrocarbons with long aliphatic chains and double/triple bonds or aromatic/alicyclic fragments. Surprisingly, in the earlier work of Kolesnikov\textsuperscript{77} no compounds with double or triple bonds were found, probably due to their hydrogenation. However, another explanation for this fact could be the higher molecular weight of propane compared with than methane or ethane, which means that the decomposition of the propane is easier with a more complex mechanism and increased number of possible chemical reactions during high thermobaric conditions.

The high fluorescence in the fingerprint zone may be also explained by the formation of ultradispersive diamonds\textsuperscript{13}. 

\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_3 & \rightarrow \text{CH}_2=\text{CH}-\text{CH}_3 + \text{H}_2 \\
\text{CH}_2=\text{CH}-\text{CH}_3 & + \cdot \text{CH}_3 \rightarrow \text{CH}_2=\cdot \text{CH}-\text{CH}_2 + \cdot \text{CH}_4 \\
\text{CH}_2=\text{C}=\text{CH}_2 & + \cdot \text{CH}_3 \rightarrow \text{CH}_2=\text{C}=\cdot \text{CH} + \cdot \text{CH}_4 \\
2 \cdot \text{CH}_2=\text{C}=\cdot \text{CH} & \rightarrow \text{C}
\end{align*}
Figure 3.7. Raman spectra of raw propane and its products after heating and pressurizing 3 GPa and $T = 900-2311$ K ($\pm 100$ K). The reference peaks for C-H valence of saturated hydrocarbon compounds were taken from $^{137-139,146}$, for unsaturated – from $^{146,147}$, for graphite (soot) modes were taken from $^{154,155}$. The reference peaks for C-C stretching and C-C bending of hydrocarbons were taken for ethane from $^{77}$, for propane from $^{77}$, for n-butane from $^{77,156}$, for n-pentane $^{157}$, for n-hexane $^{158}$. The propane remained stable at 900 K and below. The spectra of untouched propane correspond well with the previous experiments carried out by me and my research group $^{140}$. 
Figure 3.8. Raman spectra of raw propane and its products after heating and pressurizing at 6 GPa and $T = 940-1600$ K (±100 K). The reference peaks for C-H valence of saturated hydrocarbon compounds were taken from $^{137-139, 146}$, for unsaturated – from $^{146, 147}$, for graphite (soot) modes were taken from $^{154, 155}$. The reference peaks for C-C stretching and C-C bending of hydrocarbons were taken for ethane from $^{77}$, for propane from$^{77}$, for n-butane from$^{77, 156}$, for n-pentane$^{157}$, for n-hexane$^{158}$. The propane remained stable at 940 K and below. The spectra of untouched propane correspond well with the previous experiments carried out by me and my research group$^{140}$.

To sum up, it was found that various hydrocarbons could be obtained from propane reactions in the investigated range of thermobaric conditions, which are also relevant for the Earth’s mantle conditions. Propane, at extreme thermobaric conditions, is transformed into a wide range of saturated and unsaturated hydrocarbons as well as carbon in the form of graphite or soot and molecular hydrogen without any influence from catalysts and container materials.
Chapter 5. Conclusions and future work

In summary, during this thesis, the following tasks were carried out:

1) Investigation of propane's high-pressure behavior using DACs with Raman and IR spectroscopy reveals the stability of the molecule upon 40 GPa. With the help of Raman spectroscopy, it was found that propane exhibits three phase transitions at 6.4 (5), 14.5 (5) and 26.5 (5) GPa, while IR spectroscopy shows nearly the same results with three phase transitions at 7.0 (5), 14.0 (5) and 27.0 (5) GPa. Raman shifts of propane's vibrational bands change linearly with pressure increase.

2) The conducting of the butane isomers HP study shows that the butane molecule structure could not affect the phase transitions number in the pressure range of 3-40 GPa. Despite the different properties, occurrence, application, spectral representation and number of vibrational bands, both iso- and normal butane undergo two phase transitions, which were detected by means of Raman spectroscopy in DACs – 1.9 (5) and 2.9 (5) for n-butane and 2.7 (5) and 3.5 (5) for i-butane.

3) HPHT chemical transformations of propane showed that this molecule could be stable in a broad range of pressure (3-14 GPa) and temperatures <900 K, while with the increase in temperature a series of hydrocarbon compounds may be formed, including C₁-C₆ n-alkanes, hydrocarbons of complex structure with long alkyl chains, unsaturated bonds or aromatic fragments. The formation of soot or graphite or even more carbon forms was detected during the laser-heated DAC experiments. The presence of hydrogen in the Raman spectra was also detected. Occurrence and stability of various hydrocarbons in the Earth's deep interior could be a primary source of natural gas hydrates, which are contributing to the effect of global warming.
It is also a well-known fact that natural gas hydrates include in their content not only methane, but also heavier hydrocarbons, and their melting could drive the emission process. Our observations, together with that fact, lead to a thought that propane (as methane and ethane, which were investigated earlier by our research group) and probably butanes could be formed in the Earth’s asthenosphere and contribute to the formation of natural gas hydrates. That means that the sources of emissions into the atmosphere are more complicated than previously thought and not only anthropogenic factors could play a key role.

**Future investigations** will be dedicated to the following projects:

1) Investigation of high-pressure, high-temperature transformations of butane isomers and their fate in the deep carbon cycle with their influence on natural gas hydrate formation

2) Investigation of natural gas as a system of C₁-C₄ hydrocarbons and comparison of their HPHT behavior with the behavior of individual hydrocarbons in the high-pressure region

3) Implementation of various computational simulation methods for HPHT investigations of hydrocarbon behavior

4) Investigation of hydrocarbon HPHT transformations under crustal and hydrothermal conditions

5) Involvement of other high-pressure methods in the investigation of HPHT chemistry of propane and butanes

The study has the following **limitations** as well:

1) Additional data is necessary to confirm the presence of hydrogen in the pressure chamber

2) The influence of mantle surrounding on hydrocarbon behavior requires additional study
Chapter 6. Summary of appended papers

This doctoral thesis is based on four journal papers. A summary of these papers is introduced in this chapter.

**Paper A.** Raman and IR Spectroscopy Studies on Propane at Pressures of Up to 40 GPa

In this paper, Raman and IR spectroscopy was applied to study high-pressure behavior of propane at pressures of up to 40 GPa in the diamond-anvil cell. Propane exhibits three phase transitions at 6.4(5), 14.5(5), and 26.5(5) GPa in Raman spectroscopy and at 7.0(5), 14.0(5), and 27.0(5) GPa in IR spectroscopy. The results also reveal the absence of chemical transformations of propane in the pressure range mentioned above.

**Paper B.** Raman high-pressure study of butane isomers up to 40 GPa

Raman spectroscopy investigations on normal and isomeric butanes were performed at pressures of up to 40 GPa at ambient temperatures using the diamond-anvil cell technique. Normal butane undergoes two phase transitions at 1.9(5) GPa and 2.9(5) GPa and isobutane at 2.7(5) GPa and 3.5(5) GPa. As in the case of propane, butanes, of both normal and isomeric structure, show no chemical activity.

**Paper C.** Raman spectroscopy study on chemical transformations of propane at high temperatures and high pressures.

This paper is devoted to the in situ Raman spectroscopy study of propane C3H8 using laser heating technique coupled with diamond anvil cells in the range of pressures from 3-22 GPa and temperatures 900 - 3000 K. It was found that while being exposed to particular thermobaric conditions, propane could react, forming hydrocarbons and carbon. The paper also shows that propane remains stable in the earlier mentioned pressure range and temperatures <900 K.

**Paper D.** High-pressure chemistry of propane
The last paper covers an issue of propane fate while being subjected to the broad ranges of high pressures and high temperatures. The chemical mechanism of the transformations of propane is proposed. The temperature role in the high-pressure behavior of propane was examined thoroughly.
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Appendix

Calculation of total impact of light hydrocarbons C₂-C₄ on CO₂ content in the atmosphere

As for the higher hydrocarbons, the amount of CO₂ produced from the full oxidation of hydrocarbon is calculated in the same manner as was shown with the example of methane. Ethane, propane, n-butane and i-butane, while being oxidized result in 2.93, 3.0, 3.03 and 3.03 kg respectively. In summary, we get the value of 2.93 + 3 + 2*3.03 = 11.99 kg of CO₂. The obtained value of approximately 12 kg of CO₂ means that 1 kg of non-methane hydrocarbons C₂-C₄ which enter the atmosphere under the oxidation together result in 12 kg of CO₂. Taking into consideration the value of total non-methane hydrocarbon emissions, we may calculate the value of total CO₂ produced during the oxidation of NMVHCs in the atmosphere (table 1):

(19+23+22.1+14.7) *2 = 1.9 Gt of CO₂ in a year.
Paper A

Raman and IR Spectroscopy Studies on Propane at Pressures of Up to 40 GPa

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Raman and IR Spectroscopy Studies on Propane at Pressures of Up to 40 GPa

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Supporting Information

ABSTRACT: Raman and IR spectroscopy studies on propane were performed at pressures of up to 40 GPa at ambient temperatures using the diamond anvil cell technique. Propane undergoes three phase transitions at 6.4(5), 14.5(5), and 26.5(5) GPa in Raman spectroscopy and at 7.0(5), 14.0(5), and 27.0(5) GPa in IR spectroscopy. The phase transitions were identified using the Raman and IR splitting modes and the appearance or disappearance of peaks, which clearly corresponded to the changes in the frequencies of the modes as the pressure changed. Our results demonstrate the complex high-pressure behavior of solid propane.

I. INTRODUCTION

Propane (C₃H₈) is the third member of the alkane homologous series, a three-carbon, acyclic, saturated, gaseous hydrocarbon at ambient conditions, and a normal constituent of natural gas (also gas hydrates, shale, and coalbed gas) with an average content ranging from 0.1 to 7%. This compound is commonly known and widely used as an engine, blowtorch, and domestic fuel, a refrigeration agent, an aerosol propellant, and a feedstock for basic organic and petrochemical needs. Alkanes (especially light alkanes) have been found in the atmosphere of outer planets and their satellites, meteorites, comets, and other space objects. Propane is present in petroleum systems and, according to ref 6, can be detected in the atmosphere due to Earth’s degassing, anthropogenic activity, and volcanic, hydrothermal, and other geological factors. In fact, propane is the third most abundant hydrocarbon in the atmosphere after methane and ethane, with average annual emissions of approximately 10 Tg.

Numerous high-pressure studies of linear n-alkanes have been conducted over the past few years, including methane,7−9 ethane,8,10 pentane,11 hexane,12 and heptane.13 High-pressure investigations of propane have only been performed at up to 6 GPa,14 and under ambient temperatures, the polycrystalline propane undergoes a phase transition at 3.2 GPa. The wide range of thermodynamic conditions under which propane may exist on the Earth’s surfaces and interiors remains largely unexplored.

Vibrational spectroscopy is useful for studying the behavior of different compounds under high pressures, particularly for phase transitions.15−17 With vibrational spectroscopy, propane was detected in the atmosphere of Titan and Jupiter and in Saturn’s stratosphere.18,19 Here, we present a new Raman and IR spectroscopy study on propane at ambient temperatures and under pressures of up to 40 GPa.

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II. EXPERIMENTAL SECTION

Propane, 99.5% pure, from Linde Gaz Polska was used. In our experiment, propane was cryogenically loaded in symmetric BX-90-type diamond anvil cells (DAC) equipped with synthetic, CVD-type IIa diamonds with a culet size of 250 μm. The rhenium gasket was compressed to a thickness of 35 μm, and a hole 110 μm in diameter was drilled in the center to form a cylindrical sample chamber.

The Raman spectra were obtained by exciting with a He−Ne laser (632.8 nm excitation) and acquired by using a LabRam spectrometer with a 2 cm⁻¹ spectral resolution. For the pressure measurements, a ruby chip approximately 5 μm in size was placed in the samples for the pressure determinations. The obtained spectra were analyzed with OPUS v7.2.139.1294 software. The uncertainties in the Raman and IR peak positions were ±1 cm⁻¹ in both methods.

The pressure in the DAC was measured before and after the Raman or IR spectra to determine the hysteresis value in the cell. As a result, the hysteresis value does not exceed the error in the pressure measurement using the ruby luminescence line (±0.5 GPa).

Figure 1. Raman spectra of propane obtained at ambient temperatures and high pressures upon compression from 5.1(5) to 40.0(5) GPa. For clarity, the spectra have been divided into three regions: (a) 800−1300 cm⁻¹, (b) 1350−1550 cm⁻¹, and (c) 2900−3100 cm⁻¹. The 1250−1350 and 2100−2700 cm⁻¹ regions are dominated by the diamond first- and second-order peaks and are not shown. At a pressure of 6.4(5) GPa, we can see a considerable change in the spectrum appearance, especially among the symmetric skeletal C−C stretching mode v8 (~860 cm⁻¹), the CH₃ deformational modes (both symmetric and asymmetric, ~1400−1450 cm⁻¹), and the CH₃/CH₂ stretching modes (both symmetric and asymmetric) in the region of the valence vibrations (2900−3100 cm⁻¹). The low-intensity bands from different vibrational modes become more distinct when the Raman spectra of propane at 5.1(5) and 6.4 GPa(5) were compared. At 14.5(5) GPa, the doublet at ~860 cm⁻¹ further splits, and the other vibrational modes become less intense and less sharp, which can be related to the phase transition. The last observed distinct mode change appears at 26.5(5) GPa and is especially pronounced in the CH₃ deformational mode region (~1400−1450 cm⁻¹), where a strong change in the intensity ratios is seen. The same result was obtained during the decompression experiments (Figure S1). The hysteresis value does not exceed the error in the pressure measurement using the ruby luminescence line (±0.5 GPa).

II. EXPERIMENTAL SECTION

Propane, 99.5% pure, from Linde Gaz Polska was used. In our experiment, propane was cryogenically loaded in symmetric BX-90-type diamond anvil cells (DAC) equipped with synthetic, CVD-type IIa diamonds with a culet size of 250 μm. The rhenium gasket was compressed to a thickness of 35 μm, and a hole 110 μm in diameter was drilled in the center to form a cylindrical sample chamber.

The Raman spectra were obtained by exciting with a He−Ne laser (632.8 nm excitation) and acquired by using a LabRam spectrometer with a 2 cm⁻¹ spectral resolution. For the pressure measurements, a ruby chip approximately 5 μm in diameter was placed into the pressure chambers near the center of the hole, and the change in the pressure was determined by using the shift in the ruby luminescence line. The IR spectra were measured by a Bruker Vertex80v FTIR spectrometer coupled to an IRRs cope II 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 cm⁻¹. Ruby chips approximately 5 μm in size were placed in the samples for the pressure determinations. The obtained spectra were analyzed with OPUS v7.2.139.1294 software. The uncertainties in the Raman and IR peak positions were ±1 cm⁻¹ in both methods.

The pressure in the DAC was measured before and after the Raman or IR spectra to determine the hysteresis value in the cell. As a result, the hysteresis value does not exceed the error in the pressure measurement using the ruby luminescence line (±0.5 GPa). Raman and IR spectra were collected for both compression and decompression experiments to reveal the differences of propane’s phase behavior.
III. RESULTS AND DISCUSSION

Despite the simplicity of the propane molecule, its vibrations are complex, and propane possesses a relatively large number of bands. Previous spectral investigations on propane under ambient conditions identified 27 distinct vibrational modes, but no experimental studies on the spectral behavior of propane at high pressures have been conducted. Changes in the Raman or IR mode behavior with pressure are regarded as good indicators of a phase transition. The pressure dependence of the propane vibrational modes was investigated at up to ~40 GPa (from ~5 GPa directly after DAC loading and ~3 GPa upon decompression), and the results are shown in Figures 1 (Raman spectroscopy) and 2 (IR spectroscopy).

In the high-pressure cell, some of the bands are weak or cannot be detected due to overlap with the Raman band vibrations from the diamond (the 1200−1400 cm⁻¹ region is dominated by a first-order diamond peak, and the 2100−2700 cm⁻¹ region is dominated by a second-order diamond peak).

Figure 2. IR spectra of propane obtained at ambient temperatures and pressures from 3 to 42 GPa. The spectra are divided into three regions: (a) 700−1100 cm⁻¹, (b) 1350−1550 cm⁻¹, and (c) 2800−3200 cm⁻¹. Because the diamond anvils are type IIa stones (nitrogen-free diamonds) whose IR absorption bands are in the range 1800−2650 cm⁻¹ (two-phonon spectrum of the diamond), we did not consider this region. At 7.0(5) GPa, we can see a change in the CH₃ deformational mode region (1400−1450 cm⁻¹) and the CH₃/CH₂ stretching modes (both symmetric and asymmetric) in the region of the valence vibrations. The low-intensity bands of the IR modes became sharper from 6.0(5) to 7.0(5) GPa. At 14.0(5) GPa, the only observed changes were the doublet of the symmetrical C−C stretching merging at ~930 cm⁻¹. The last phase transition was at 27.0(5) GPa and manifested as the CH₃ deformational mode splitting into a doublet (~1500 cm⁻¹) and was followed by the appearance of distinct modes at higher pressures. The same result was obtained during the decompression experiments (Figure S2). The hysteresis value does not exceed the error in the pressure measurement using the ruby luminescence line (~±0.5 GPa).

Figure 3. Raman modes associated with skeletal C−C stretching as a function of pressure, symmetrical (left) and asymmetrical (right). The uncertainties in the peak positions (~±1 cm⁻¹) and pressure measurements (~±0.5 GPa) were relatively small and are located within the symbols.
Moreover, the low-frequency modes are very weak in the Raman and IR spectra. In addition, a large Rayleigh background made it difficult to observe any Raman modes below 300 cm\(^{-1}\). As in almost all linear alkanes, the strongest bands in the propane molecule are the methyl (CH\(_3\)) and methylene (CH\(_2\)) stretching modes (2800–3200 cm\(^{-1}\)), the CH\(_3\) and CH\(_2\) bending modes (1400–1500 cm\(^{-1}\)), and the C–C skeletal stretching modes (∼870 cm\(^{-1}\)/1057 cm\(^{-1}\)).

In this study, we classified the Raman and IR modes of propane into several regions:

1. C–C Skeletal Stretching Region and CH\(_2\)/CH\(_3\) Rocking Region (700–1300 cm\(^{-1}\)). The 700–1300 cm\(^{-1}\) region is occupied by the IR and Raman modes associated with the symmetric and asymmetric skeletal stretching of the C–C bonds (\(\nu_8\) and \(\nu_{20}\) respectively) and the CH\(_3\) and CH\(_2\) rocking modes (\(\nu_{7}, \nu_{7_5}, \text{ and } \nu_{26}\) respectively). Figures 3 and 4 show the pressure dependence of these modes. In the Raman spectra, only two broad bands were observed at a pressure of 5.1(5) GPa, but as the pressure increased, \(\nu_8\) split into a doublet and triplet at 6.4(5) and 8.7(5) GPa, respectively, with a dramatic increase in the intensity.

Figure 4. IR modes associated with the skeletal C–C stretching and combinational modes as a function of pressure. The uncertainties in the peak positions (±1 cm\(^{-1}\)) and pressure measurements (±0.5 GPa) were relatively small and located within the symbols.

Figure 5. Vibrational modes associated with the CH\(_3\) rocking as a function of pressure. (The Raman spectrum is on the left, and the IR is on the right.) The uncertainties in the peak positions (±1 cm\(^{-1}\)) and pressure measurements (±0.5 GPa) were relatively small and are located within the symbols.

Figure 6. IR modes associated with the CH\(_2\) rocking as a function of pressure. The uncertainties in the peak positions (±1 cm\(^{-1}\)) and pressure measurements (±0.5 GPa) were relatively small and are located within the symbols.

Figure 7. CH\(_2\) and CH\(_3\) Raman bending modes as a function of pressure. The uncertainties in the peak positions (±1 cm\(^{-1}\)) and pressure measurements (±0.5 GPa) are relatively small and located within the symbols.
Starting at 17.8(5) GPa, we noticed a change in the intensity ratio. For the asymmetric skeletal C−C stretch, the doublet appears at 8.7(5) GPa and disappears at 20.5(5) GPa. At greater pressures, no significant changes were noticed in this region.

However, when analyzing the IR spectra of propane (Figure 4 shows the pressure dependence of these modes), we observed that the symmetrical C−C stretching (ν8) doublet merge into one band at 15.5(5) GPa. Another difference from the Raman spectra was seen in the 1000−1100 cm\(^{-1}\) region, where the asymmetrical C−C skeletal stretching should be located. At 1015 and 1094 cm\(^{-1}\), there are two weak bands that are not related to a particular vibration, and they could be combinational modes or overtones. According to ref 21, the asymmetric C−C skeletal stretching mode is too weak in the IR spectra, and we did not observe this vibration.

The CH\(_3\) rocking modes and C−C skeletal stretching are always discussed together\(^{24}\) because they have overlapping frequency ranges, which make it hard to distinguish the type of mode to take into account when this region is analyzed. Nevertheless, we observed a symmetric CH\(_3\) rocking mode with a medium intensity (ν7) in the 1150−1200 cm\(^{-1}\) region, and no significant changes were observed during the pressure increase, as shown in Figure 5.

The band with a wavenumber of \(\sim\)750 cm\(^{-1}\) is probably associated with the CH\(_2\) rocking mode. This type of vibration is Raman inactive; however, it appears in the IR spectra of propane at up to 40.0(5) GPa (Figure 6). No substantial changes in the band were noticed as the pressure increased.

2. Methyl Bending Region (1400−1500 cm\(^{-1}\)). Every n-alkane has a ~CH\(_2\) bending mode region at approximately 1400−1500 cm\(^{-1}\). Figure 7 shows the pressure dependence of this region. In the case of propane, this interval is characterized by the strong (ν11), asymmetric CH\(_3\) deformational mode centered at 1452 cm\(^{-1}\) overlapping with a broad structure generated by the interactions among several weaker transitions, including the CH\(_3\) deformation modes (ν16, ν17, and ν24), the CH\(_2\) scissor mode (ν5), and overtones and combination modes. Moreover, the symmetric CH\(_3\) deformations are present at the smaller wavenumbers (ν18 and ν6), but at atmospheric pressure, the bands are usually missing. With the pressure increase, we...
observed the appearance of some new bands in the region before the CH$_3$ asymmetric deformations. The bands can be referred to as symmetric CH$_3$ vibrations with a maximum intensity at 10.8 GPa, and they disappeared at higher pressures. Considering the IR spectra in this region, it can be seen that the CH$_3$ deformational modes have relatively strong intensities ($\nu_{24}$, $\nu_{4}$, $\nu_{17}$). Starting at 7 GPa, the main band splits into a doublet, and it splits into a triplet at 10.5(5) GPa (Figure 8). The strong Raman CH$_3$ deformational mode, $\nu_{11}$, which always overlaps with the CH$_2$ scissoring, $\nu_{5}$, is usually missing on the IR spectra, but the symmetric CH$_3$ rocking modes ($\nu_{6}$ and $\nu_{18}$), which are extrinsic in Raman spectroscopy, are common in IR (Figure 9).

3. CH$_3$ and CH$_2$ Stretching Region (2800–3200 cm$^{-1}$).

The region of valence vibrations or the C–H stretching region is influenced by large intramolecular interactions and interactions between the fundamental symmetric C–H stretching and the overtone of the >CH$_2$ scissor mode. In the case of propane, we observed only one broad mode at 5.1(5) GPa, and the type of the mode was difficult to identify because of overlapping. When the phase transition in propane occurred at a pressure of 6.4(5) GPa, the spectra became more complex because of the interactions between the asymmetric stretching modes $\nu_{10}$, $\nu_{14}$, $\nu_{22}$, and $\nu_{1}$ (2967, 2968, 2973, and 2977 cm$^{-1}$) of CH$_3$, with the CH$_2$ stretching modes, $\nu_{3}$ (2962 cm$^{-1}$, symmetric) and $\nu_{23}$ (2968 cm$^{-1}$, asymmetric), and several combination and overtone modes. It is important to mention that there is one more asymmetrical stretching mode of CH$_3$ $\nu_{16}$ which is always overlapped by $\nu_{1}$ (CH$_3$ symmetric stretching mode) and can be regarded as a combinational mode, $\nu_{1} + \nu_{16}$. Figure 10 shows the pressure dependence of these modes. The combinational mode of $\nu_{1} + \nu_{16}$ (CH$_3$ symmetric and CH$_3$ asymmetric stretching modes) remains distinct and intense during the pressure increase to 40 GPa. Other modes are difficult to identify as a particular type because of the close values of their Raman shifts. Some of the modes disappear as the pressure increases, and others appear in a new location of the region. The structure of the spectra in this range changes three times, which can be an indicator of three solid–solid phase transitions (6.0(5), 14.0(5) and 26.0(5) GPa).

For the analysis in the C–H vibration region, both Raman and IR spectroscopy should be applied because only the $\nu_{2}$ mode (symmetric CH$_3$ stretching mode) is present in both the Raman and IR spectra (Figure 11). The infrared-active vibrations (and their combinations) in the investigated interval are $\nu_{22}$ (asymmetric CH$_3$ stretching mode), $\nu_{16}$ and $\nu_{2}$ (symmetric CH$_3$ stretching mode), $\nu_{15}$ (asymmetric CH$_3$ stretching mode), and $\nu_{23}$ (asymmetric CH$_2$ stretching mode). Only seven C–H vibrations are assigned to the propane molecule, and $\nu_{15}$ and $\nu_{13}$ have the same wavenumbers as $\nu_{3}$ and $\nu_{16}$.

At 10.5(5) GPa, the $\nu_{16}$ mode disappeared, and another nearby mode, which probably consists of several vibrations, split into three peaks at a pressure of 7.0(S) GPa. This transformation could be due to the phase transition of propane from a liquid to a solid. Another indicator of a phase transition in propane at 7.0(S) GPa is depletion of the doublet of the
Table 1. Brief Characteristics of the Phase Transitions Determined by Vibrational Spectroscopy for the First Three Members of the Alkane Homologous Series

<table>
<thead>
<tr>
<th>hydrocarbon</th>
<th>Raman</th>
<th>IR</th>
</tr>
</thead>
<tbody>
<tr>
<td>methane</td>
<td>liquid−solid (phase I, fcc) 1.7 GPa; phase I−phase A (rhombohedral structure or tetragonal structure) at 5.3 GPa; phase A−phase B (cubic or hcp) at 10.0−18.0 GPa; phase B−phase HP (cubic or hcp) at 25.0 GPa; phase HP−phase HP at 37.0 GPa; phase HP−phase HP at 62.0 GPa;</td>
<td>liquid−solid (phase I, fcc) 1.7 GPa; phase I−phase A (rhombohedral structure or tetragonal structure) at 3.2 GPa; phase A−phase B (cubic or hcp) at 10.0−18.0 GPa; phase B−phase HP (cubic or hcp) at 25.0 GPa; phase HP−phase HP at 37.0 GPa; phase HP−phase HP at 62.0 GPa;</td>
</tr>
<tr>
<td>ethane</td>
<td>liquid−solid at 2.5 GPa; solid−solid at 3.3 GPa</td>
<td>solid−solid at 6.4 GPa(5); solid−solid at 14.5(5) GPa; solid−solid at 27.0(5) GPa</td>
</tr>
<tr>
<td>propane$^*$</td>
<td>solid−solid at 3.2 GPa;</td>
<td>solid−solid at 7.0(5); solid−solid at 14.0(5); solid−solid at 27.0(5);</td>
</tr>
</tbody>
</table>

$^*$ Liquid−solid phase transition at 3.2 GPa was determined by X-ray diffraction.

~3020 cm$^{-1}$ vibrational mode, which was the highest intensity peak at lower pressures.

The phase diagram outlined for propane is shown in Figure 12.

IV. CONCLUSIONS

In summary, high-pressure Raman and IR spectroscopic studies on propane were conducted in the range from ∼3 to slightly over 40 GPa. During the investigation, it was determined that propane molecules undergo 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. The Raman and IR behavior of propane was reported, discussed, and compared to methane and ethane spectroscopic studies (Table 1). The phase transitions affect the behavior of the vibrational mode in the same way as in lighter alkanes. For the vibrational modes of propane, 20 out of 27 modes were observed and identified on the spectra, and their pressure dependence was followed at up to 40 GPa.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.7b05492.

Raman and IR spectra (PDF)

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Author Contributions

V.K. and L.D. designed the study. L.D. designed the experiments. D.K., A.S., E.M., and L.D. carried out the experiments and analyzed the data. A.S. and B.G. helped with synchrotron experiments. D.K., E.M., V.K., A.K., and A.S. wrote the manuscript with substantial contributions made by L.D. All authors discussed the results and implications and commented on the manuscript.

Notes

The authors declare no competing financial interest.

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Author Contributions

V.K. and L.D. designed the study. L.D. designed the experiments. D.K., A.S., E.M., and L.D. carried out the experiments and analyzed the data. A.S. and B.G. helped with synchrotron experiments. D.K., E.M., V.K., A.K., and A.S. wrote the manuscript with substantial contributions made by L.D. All authors discussed the results and implications and commented on the manuscript.

Notes

The authors declare no competing financial interest.
Paper B
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Raman high-pressure study of butane isomers up to 40 GPa

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Raman high-pressure study of butane isomers up to 40 GPa

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Raman spectroscopy studies on \( n \) and \( i \)-butane were performed at pressures of up to 40 GPa at ambient temperatures using the DAC technique. Normal butane undergoes two phase transitions at 1.9(5) GPa and 2.9(5) GPa and isobutane at 2.7(5) GPa and 3.5(5) GPa. These phase transitions were identified based on observations of the splitting Raman modes and the appearance or disappearance of particular Raman peaks. Our results demonstrate the complex, high-pressure behavior of butane isomers. © 2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5049481

I. INTRODUCTION

Butane is a gaseous saturated hydrocarbon, the fourth member of the alkane homologous series, with a molecular formulae \( \text{C}_4\text{H}_{10} \) and two structural isomers – normal butane (unbranched) and isobutane (or 2-methylpropane). Due to their different structure, these two isomers are totally different as concerns chemical and physical properties as well as their different occurrence and application in industry.

Despite the number of differences, both butanes experience high levels of petrochemical demand and are present not only in the natural gas, but are found in various geological settings,1 Earth’s atmosphere2,3 and also potentially could be found on outer planets and their satellites.4,5 Raman spectroscopy is a feasible, non-destructive method for the examination of organic compounds which offers both qualitative and quantitative studies, as well as information about phase behaviour of molecules and their conformational equilibria.6–8 High-pressure examinations of butanes would also clarify the problem of petroleum systems in the Earth’s interior, their generation and retention in the geological structures.

Several spectroscopical studies of butanes were conducted in the middle of previous century,9–12 including a deep and careful analysis of conformational isomers and the difference between isobutane and butane vibrational bands, but no high-pressure studies were performed, except the work13 where butane was studied up to 5 GPa. Surprisingly, butane is the last light alkane to be examined with the use of high-pressure techniques, while methane,14–16 ethane17 and propane13,18 have been studied extensively. It is important to note that higher n-alkanes (\( \text{C}_5 \)- \( \text{C}_7 \)) were also studied several times using diamond anvil cell (DAC)/Raman spectroscopy techniques.19–21 The increasing interest in hydrocarbon occurrence in the universe and origin of this group of compounds makes this study beneficial. Here, we present a paper which focuses on Raman spectroscopy study of butanes at ambient temperatures and under pressures of up to 40 GPa with some modifications of the previous assignments.

II. EXPERIMENTAL SECTION

\( n \)-Butane and isobutane, both 99.95% pure, from Riessner Gase GmbH were used during the examination with no additional purification. In our experiment, butanes were cryogenically loaded in
symmetric BX-90-type diamond anvil cells (DAC) equipped with synthetic, CVD-type IIa diamonds with a culet size of 250 µm. The rhenium gasket was compressed to a thickness of 35 µm. With the help of laser techniques, a hole of 110 µm in diameter was drilled in the center to form a cylindrical sample chamber. The Raman spectra were obtained by exciting with a He-Ne laser (632.8 nm excitation) and acquired using a LabRam spectrometer with 2 cm\(^{-1}\) spectral resolution. For pressure determination, a ruby chip approximately 5 µm in diameter was placed into the pressure chamber near the center of the hole, and the change in the pressure was determined using the shift in the ruby luminescence line. The uncertainties in the Raman peak positions were ±1 cm\(^{-1}\). A decision was taken to measure the pressure in the DAC before and after the collection of the Raman spectra in order to determine the hysteresis value in the cell. As a result, the hysteresis value does not exceed the error in the pressure measurement using the ruby luminescence line (±0.5 GPa). Raman spectra were collected both for compression and decompression experiments to reveal the differences in the butanes’ phase behavior.

To avoid the wrong interpretation of results, Raman spectra were collected in three different places in the pressure chamber.

III. RESULTS AND DISCUSSION

In Raman spectra of hydro-carbons the most useful information is located at the 3200-2800 and 1700-300 cm\(^{-1}\) regions. Raman spectra of n-alkanes have presumably the same representation due to the methyl (-CH\(_3\)) and methylene (-CH\(_2\)-) bands – on the contrary, Raman spectra of n-alkanes and isoalkanes show a strong difference because of the branched character of the latter. Another major difference between normal and isobutane which could be seen on spectra is that n-butane is the simplest hydrocarbon in which rotational isomerism occurs. Normal butane introduces an additional possibility that the carbon skeleton could lead to the existence of more than one configuration due to rotation around the C-C bonds. The problem of the influence of molecular conformation on spectral properties of organic compounds (especially normal paraffins) has earned a certain interest among scientists,\(^{22,23}\) moreover, vibrational spectroscopy provides the broadest data on conformational isomers’ behaviour. It is common knowledge that hydrostatic pressure affects the changes of the intra and intermolecular forces. Furthermore, the conformational changes in the high-pressure region plays a certain role in the investigation of different phenomena observed in the science of high-molecular compounds and polymers, especially in the biological field.\(^{22,23}\) Butane has three conformers with a difference in the C-C-C-C torsion angle – one trans (or anti) and two gauche (mirror images). As stated in some studies, several lines of gauche forms in the Raman spectra of liquid alkanes disappear during the solidification because of the reversion to the trans form in the crystal state – which could be useful for study of lipid bilayer systems.\(^{24}\) Of beneficial importance is the fact that the spectral investigations indicate that each configuration of n-butane has its own set of vibrational frequencies.

Combining all of the experimental and calculated data it could be concluded that the butane molecule possesses 36 distinct vibrational modes, but no experimental studies have been done in the high-pressure region. Moreover, spectroscopical study of butane’s high-pressure behaviour has never been performed, furthermore the interpretation of solid butane’s spectra could be a challenging task due to weaker lines and scattering background. As could be seen from the Raman work (Figure 1) no single configuration of n-butane will fit the spectra, since many more lines are observed than are to be expected.

Theoretically, isobutane also possesses 36 distinct vibrational modes, but according to the recorded spectra, there are notable differences in n-butane in all of the 3 regions (Figure 2), mentioned previously. This difference could be explained by symmetry of the i-butane molecule which leads to the degeneration of several vibrations. For example, in the region of C-H stretching vibrations (2800-3300 cm\(^{-1}\)), vibrations of iso-butane are more distinct because of -CH\(_3\) fragment domination in the molecule (the same assessment applies to CH\(_3\) bending region). The vibrations from the region of 1100-1300 cm\(^{-1}\) of isobutane are more intense and release in the triplet while n-butane gives only singlet in this diapason – this is due to the complicated interaction of tert-butyl fragments in isobutane. Tertiary wagging of isobutane (v\(_{15}\)) is another striking difference of these compounds. Isobutane has a significantly smaller number of vibrations on the spectra that normal butane because of the absence
FIG. 1. Raman spectra of normal butane obtained at ambient temperature and at high pressures upon compression from 1.4(5) to 40.2(5) GPa. For clarity, the spectra have been divided into three regions: (a) 300-1300 cm$^{-1}$ (C-C stretching and methyl rocking region), (b) 1400-1600 cm$^{-1}$ (methyl bending region), and (c) 2800-3300 cm$^{-1}$ (C-H stretching region). The 1250-1350 cm$^{-1}$ and 2100-2700 cm$^{-1}$ regions are dominated by diamond first-second-order peaks and have not been shown. As it could be seen from the spectra, the specific vibrations of gauche-form have totally disappeared starting from the 3.6(5) GPa, which shows the phase transition and total solidification of n-butane. At pressures between 1.9(5) and 2.4(5) GPa we can see a considerable change of spectrum appearance, especially in the 2800-3300 cm$^{-1}$ region, where all the C-H stretching vibrations became blurred in comparison with 1.4(5) GPa. This phase transition was also discovered in this paper using XRD technique at 1.8 GPa. Another phase transition has appeared in the region between 2.4(5) and 2.9(5) GPa, where we can see double splitting of $v_{11}$ mode, dramatic increase of $v_{10}$ and $v_9$ intensity, the disappearance of $v_{14g}$ and $v_{32g}$ modes, while in the region of CH$_3$ bending region, a number of peaks became distinct. The decompression spectra of n-butane also show good correspondence with the compression experiment (see supplementary material S1).

of its conformational isomers. The mode assignments of normal and isobutane were based on the following studies.$^{6,7,10,11,25–27}$

From the vibrational assignments of the simpler molecules from the alkane homologous series such as methane, ethane and propane and from a comparative examination of the spectra of a large number of other organic molecules, certain general frequency regions have come to be recognized.

In this study, we classify the Raman modes of butanes into several regions.

**A. C-C-C deformation (longitudinal acoustic mode < 650 cm$^{-1}$)**

This region of spectra is quite weak in the case of n-alkanes both in the liquid and solid phases however, while performing the measurement, it was possible to record several vibrations. According to Ref. 11 this region is dominated by two peaks of C-C-C bending, one for trans configuration ($v_{11}$ 430.1 cm$^{-1}$) and one for gauche (319.5 cm$^{-1}$ $v_{17}$) however, we observed only trans-configuration peak, which is splitting to two bands after the second phase transition (Fig. 3). As for the isobutane, it is expected that this molecule has two deformational vibrations – symmetrical and unsymmetrical ($v_8$ and $v_{19}$ respectively), but during the current study only $v_{19}$ was found on the spectra.

**B. C-C skeletal stretching region and CH/CH$_2$/CH$_3$ rocking region (600-1350 cm$^{-1}$)**

In the region in which the skeletal stretching vibrations of normal paraffins are expected (approximately between 700 to 1100 cm$^{-1}$) n-butane has two bands of appreciable intensity – $v_{10}$ ($v_{15}$ for gauche) and $v_9$ ($v_{13}$ for gauche). Relatively strong $v_{15}$ and $v_{13}$ Raman mode in the liquid state suggests that gauche rotamer is present only in the liquid state. The disappearance of these modes with the phase transition and increase in intensity of $v_{10}$ and $v_9$ mode suggest that n-butane in the condensed
FIG. 2. Raman spectra of isobutane obtained at ambient temperature and at high pressures upon compression from 1.6(5) to 37.6(5) GPa. For clarity the spectra have been divided into three regions: (a) 300-1300 cm\(^{-1}\) (C-C stretching and methyl rocking region), (b) 1400-1600 cm\(^{-1}\) (methyl bending region), and (c) 2800-3300 cm\(^{-1}\) (C-H stretching region). The 1250-1350 cm\(^{-1}\) and 2100-2700 cm\(^{-1}\) regions are dominated by diamond first-second-order peaks and have not been shown. The spectra of isobutane demonstrate several phase transitions – at pressure between 1.6(5) and 2.7(5) GPa the region of C-H stretching became less sharp, the same as in the region of methyl bending. Another phase transition was noted in the interval from 2.7(5) to 3.5(5) GPa where the spectrum changes dramatically – methyl bending vibrations became sharp and distinct, while \(v_6\) and \(v_{16}\) change its structure from triplet to doublet. With pressure increase no substantial changes were registered. As it could be seen from the spectra, the specific vibrations of gauche-form totally disappear starting from 3.6(5) GPa, which shows the phase transition and total solidification of i-butane. The decompression spectra of isobutane also correspond well with the compression experiment (See the supplementary material S2).

phase (like all n-alkanes) prefers to be in trans conformation. Moreover, based on the following study\(^\text{27}\) in the whole region (until the first-order diamond peak) seven fundamentals are allowed in the Raman spectrum including two further types of vibration, C-C stretching vibrations and motions involving changes of HCC angles. One of the most representative vibration is C-C stretching mode \(v_{10}\), located at the value of 840 cm\(^{-1}\). At the liquid state the same vibration of the gauche-configuration could also be observed (~830 cm\(^{-1}\)) which disappears with the phase transition (Figure 4). At the value of 3.6 GPa, this peak splits to the doublet, but with the pressure increase only the singlet was presented on the spectra. Another C-C stretching vibration \(v_9\) (\(v_{13}\) for gauche) is located at

FIG. 3. The Raman modes of n-butane (left) and i-butane (right) associated with the deformational C-C-C bending as a function of pressure.
~1060 cm$^{-1}$ and has weaker intensity than $v_{10}$. The C-C stretching of isobutane is represented by $v_7$ and $v_{18}$ non-degenerate skeletal vibrations with no substantial changes during the pressure increase (Figure 5).

When moving to the methyl rocking frequencies, two observations could be noted directly:

1. While examining n-butane and higher n-paraffins, the terminal CH$_3$ groups are strongly separated so that very minor interaction between them is to be expected that makes symmetric and antisymmetric vibrations indistinguishable, and very little separation in their frequencies will occur.

2. Secondly, the studies on propane$^6,12,18$ show that the difference to be expected between in-plane and out-of-plane CH$_3$ rocking frequencies is small (~20 cm$^{-1}$).

The band which was noticed on the spectra around ~800 cm$^{-1}$ (Figure 6) could possibly be assigned to the CH$_2$-rocking mode.$^7$ Another viewpoint on this vibration is that it is caused by skeletal vibrations of non-planar forms and not to CH$_2$ rocking vibrations.$^{10}$

CH$_3$-rocking modes of gauche-conformation are presented in the low-pressure region only (Figure 7) of the spectra which indicates the solidification of n-butane, on the contrary, the CH$_3$-rocking of trans-conformation is presented all over the spectra with no substantial changes with pressure increase. CH$_3$-rocking of isobutane possesses many more frequencies than n-butane due to complex CH$_3$-interactions in the tert-butyl group (Figure 8).
FIG. 6. The Raman modes associated with the CH$_2$-rocking mode ($v_{25}$) as a function of pressure.

FIG. 7. The Raman modes associated with the $v_{14}$, $v_{32}$, $v_{33}$ CH$_3$ rocking of gauche-n-butane as a function of pressure (left) and $v_8$ of trans-n-butane(right).

CH$_2$-twisting modes (Figure 9) of n-butane are located closely to a diamond first-order peak and strating from 14 GPa, the intense diamond band is overlapping in this mode, however in the low-pressure region we could see a disappearance of the gauche vibrational mode, while the trans mode could be distinguished until the overlapping of the diamond mode.

C. Methyl bending region (1350-1600 cm$^{-1}$)

Butane’s methyl bending mode region lays between 1400-1600 cm$^{-1}$. Because of the complex interaction between CH$_3$ asymmetric and symmetric deformational modes and CH$_2$ scissoring, it

FIG. 8. The Raman modes associated with the CH$_3$ wagging/rocking mode ($v_{6+16}$) of iso-butane as a function of pressure.
could be difficult to refer each band to a particular mode. In the case of n-butane, this interval is characterized by intense asymmetric CH$_3$ deformational mode centered at $\sim$1460 cm$^{-1}$. After total solidification of n-butane the intensities of the bands in this region were decreased. Isobutane, on the contrary, here has a relatively high number of vibrational frequencies which are due to three –CH$_3$ fragments in the molecule, which is why isobutane’s spectra are rich with various CH$_3$ vibrations and their combinational modes (Figures 10–13).

FIG. 9. The Raman modes associated with the CH$_2$ twisting mode ($v_{23}$ trans and $v_{11}$ gauche) of n-butane as a function of pressure.

FIG. 10. The Raman modes associated with the CH$_3$ symmetrical deformation mode ($v_6$) of n-butane (left) and ($v_{14}$) of iso-butane (right) as a function of pressure.

FIG. 11. The Raman modes associated with the CH$_3$ asymmetrical deformation mode ($v_{12}$) of n-butane as a function of pressure.
The last vibration which should be considered is the tertiary wagging (Figure 14). The double degenerate CH-rocking mode of isobutane is a subject of doubt among alkane spectroscopical studies – this mode has been attributed to 900 cm\(^{-1}\)\(^{110}\) or to 1200 cm\(^{-1}\) and 1095 cm\(^{-1}\)\(^{12}\), but none of them were
found on the spectra obtained. Based on the previous investigation of propane, the CH\textsubscript{2} wagging mode was found at the value of \( \sim 1330 \text{ cm}^{-1} \), the same mode of isobutane \((v_{15})\) mode could possibly give a singlet at the value of \( \sim 1340 \text{ cm}^{-1} \) which is splitting to the doublet at a pressure of 6.0 (5) GPa and then returning to the singlet type of peak starting from 11.9 (5) GPa.

D. C-H stretching region

The complex vibrations involving principally the stretching of C-H bonds give rise to several Raman shifts in the diapason from 2800 to 3200 cm\(^{-1}\). However, these butane vibrations are not that distinguishable (Figure 15), nevertheless, in terms of this study it was possible to find four types of stretching – methyl symmetric \((v_2)\)\ symmetric\((v_{21}+v_1)\) and methylene symmetric\' asymmetric\((v_{13}+v_{21})\). Unfortunately, strong interaction of modes and various overtones and combinational modes make these frequencies difficult to resolve.

The Raman vibrations in this region (Figure 16) have a striking contrast with n-butane’s spectra first of all because of the absence of methylene vibrations in the case of isobutane, instead of a \(-\text{CH}_2\) bond on the spectra of iso-butane, the tertiary CH bond appears.

The phase diagrams outlined for n-butane is shown in Fig. 17. The data presented on the following figure was obtained from various papers and handbooks aimed to investigate different
properties of the n-butane molecules.\textsuperscript{13,28–30,37} Unfortunately, isobutane’s phase behavior was studied no so extensively as n-butane’s that’s why the phase diagram in the high-pressure region wasn’t developed.

IV. CONCLUSION

In summary, high pressure Raman spectroscopic studies on normal and isobutane were conducted in the range of up to 40 GPa. It was found that n-butane undergoes two phase transitions at 1.9 (5) GPa and 2.9 (5) GPa as well as i-butane undergoes the same number of phase transitions at 2.7 (5) GPa and 3.5 (5) GPa respectively. The Raman behavior of butane isomers was reported, discussed and compared to other alkane spectroscopical studies (Table I). The table includes only the data on phase transitions which are occurring at room temperature, while the data on high-pressure and high temperature studies is presented in the review of Kolesnikov et. al.\textsuperscript{36}

As could be seen, the phase transitions affect the behavior of the vibrational mode in the same way as in lighter or higher alkanes\textsuperscript{31–35,37} (Table I). For all of the alkanes mentioned in the table the following statement could be made - Raman bands gradually shifted to higher frequencies with increasing pressure because of reduction in bond length and atomic distances under higher pressure. Starting from butanes after the first phase transition all of the modes attributed to the gauche conformations totally or partially disappeared with the pressure increasement. The best indicators for phase transitions are the modes from C-C stretching and C-H stretching region, first of all due to they high intensity as well as to simplicity and evidence of the changes with the phase transitions.

It was found that isomeric structure in the case of butanes does not affect the number or character of phase transitions. Moreover, it could be concluded, that no correlation was observed between the length of the hydrocarbon chain and the quantity of phase transitions. Isobutane’s and normal butane’s spectra were compared at a whole range of pressures, the difference between these two compounds has been saved during the pressure increase.
<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Raman Spectroscopy</th>
<th>Infrared Spectroscopy</th>
<th>Other methods (mostly XRD)</th>
<th>Additional information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>1) liquid-solid (phase I, fcc) 1.7 GPa;</td>
<td>1) liquid-solid (phase I, fcc) 1.7 GPa;</td>
<td>1) Phase I- Phase A ~5 GPa</td>
<td>Each of these phase transitions could be clearly observed by the change of C–H symmetric stretching mode, $v_1$ (both for Raman and IR) or $v_3$ asymmetric stretching mode; for example, the A-B phase transition could be seen by splitting of the C–H symmetric stretching mode, $v_1$, in the Raman and IR spectra.</td>
</tr>
<tr>
<td></td>
<td>2) phase I - phase A (rhombohedral structure or tetragonal structure) 5.2 GPa; phase A - phase B (cubic or hcp) 10–18 GPa;</td>
<td>2) phase I - phase A (rhombohedral structure or tetragonal structure) 5.2 GPa;</td>
<td>2) Phase A – Phase B ~10 GPa</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3) pre-B phase with structure close to phase B but rotation of molecules close to the phase A ~12 GPa;</td>
<td>3) phase A - phase B (cubic or hcp) 10–18 GPa;</td>
<td>3) Phase A - Phase B 19 GPa</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4) phase B - phase $\beta$ (cubic or hcp) 25 GPa;</td>
<td>4) phase B - phase $\beta$ (cubic or hcp) 25 GPa;</td>
<td>4) Phase SC (simple cubic) – Phase cHP 69-94 GPa</td>
<td></td>
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<tr>
<td></td>
<td>5) phase $\beta$ – phase $\beta_3$ 37 GPa;</td>
<td>5) phase $\beta_3$ – phase $\beta_2$ 37 GPa;</td>
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<tr>
<td></td>
<td>6) phase $\beta_2$ – phase $\beta_3$ 62 GPa,14</td>
<td>6) phase $\beta_2$ – phase $\beta_3$ 62 GPa,14</td>
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<td></td>
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<tr>
<td></td>
<td>7) Phase SC (simple cubic) – Phase $\beta$ cHP 75-80 GPa,16</td>
<td>7) Phase SC (simple cubic) – Phase $\beta$ cHP 75-80 GPa,16</td>
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<tr>
<td></td>
<td>8) Phase $\beta$ cHP - new Phase (rearrangement/orientation of the methane molecules within the framework of the cubic lattice)11</td>
<td>8) Phase $\beta$ cHP - new Phase (rearrangement/orientation of the methane molecules within the framework of the cubic lattice)11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethane</td>
<td>1) liquid-solid 2.5 GPa;</td>
<td>-</td>
<td>-</td>
<td>1) $v_3$ C-C stretching splitting, $v_{11}$ CH$<em>3$ bending increasing in intensity, appearing of two more peaks. $v</em>{10}$ CH$_3$ stretching from weak shoulder to two sharp peaks.</td>
</tr>
<tr>
<td></td>
<td>2) solid-solid 3.3 GPa</td>
<td>2) solid-solid 3.3 GPa</td>
<td></td>
<td>2) $v_{13}$ CH$<em>3$ bending increasing in intensity, the three peaks became sharper. $v</em>{10}$ CH$_3$ stretching increasing in intensity of the first peak and more sharp splitting with the second peak, appeared during liquid-solid phase transition. As stated in Ref. 17 other ethane frequencies are less or more insensitive to the pressure increase.</td>
</tr>
<tr>
<td>Substance</td>
<td>Phase Transition 1</td>
<td>Phase Transition 2</td>
<td>Phase Transition 3</td>
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<tr>
<td>Propane</td>
<td>1) solid-solid 6.4(5) GPa;</td>
<td>1) solid-solid at 7.0(5) GPa;</td>
<td>1) liquid-solid 3.2 GPa;</td>
<td></td>
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<tr>
<td></td>
<td>2) solid-solid 14.5(5) GPa;</td>
<td>2) solid-solid at 14.0(5) GPa;</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3) solid-solid 27.0(5) GPa;</td>
<td>3) solid-solid at 27.0(5) GPa;</td>
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<td></td>
</tr>
<tr>
<td>Butane</td>
<td>This study:</td>
<td>1) liquid-solid 1.9 (5) GPa</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1) liquid-solid 1.9 (5) GPa</td>
<td>-</td>
<td>1) liquid-solid 1.8 GPa;</td>
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</tr>
<tr>
<td>iso-Butane</td>
<td>This study:</td>
<td>1) liquid-solid 2.7 (5) GPa</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2) solid-solid 2.9 (5) GPa</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-pentane</td>
<td>1) liquid-solid transition ∼ 2.5 GPa;</td>
<td>1) liquid-solid transition ∼ 2.5 GPa;</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2) liquid-solid transition ∼ 3.0 GPa;</td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>3) solid-solid transition ∼ 12.3 GPa;</td>
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</tbody>
</table>

The information about spectroscopic behavior of butane isomers and their phase transitions were described in detail in the present paper.

A strong C-C stretching (1090 cm⁻¹) mode in the liquid state suggests that large numbers of gauche rotamers are present in the liquid state but with the phase transition it disappears, while C-C stretching mode increases in its intensity (1130 cm⁻¹) and another mode appears at 1060 cm⁻¹.

2) Disappearance of C-C-C Angle Bending (300 cm⁻¹), CH₂-rocking (895 cm⁻¹). Increase of the trans modes intensity with the pressure increase in the region of C-H stretching.
<table>
<thead>
<tr>
<th>Substance</th>
<th>Liquid-solids transition 1</th>
<th>Liquid-solids transition 2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>n-hexane</strong></td>
<td>1) liquid-solid $\sim$ 1.4 GPa$^{14}$</td>
<td>2) solid-solid $\sim$ 9.1 GPa$^{20}$</td>
</tr>
<tr>
<td></td>
<td>1) The spectrum of CH$_2$-CH$_3$ bending at 1.4 GPa is sharper, more intense, and has more split bands than the other one, below 1.4 GPa. Strong change in the frequency of acoustic mode at 328 cm$^{-1}$. CH$_3$-rocking mode splits into doublet (908 cm$^{-1}$).</td>
<td>2) Acoustic mode (328 cm$^{-1}$ ) and CH$_3$-rocking mode (908 cm$^{-1}$) reduces in its intensity and disappears above 9.1 GPa. In the region of Skeletal C-C Stretching Region all of the gauche-conformers modes are disappearing. Change in the slope in the CH$_2$-CH$_3$ bending region. In the CH$_2$-CH$_3$ stretching region a considerable mode broadening as well as changes in their intensity ratio could be observed.</td>
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</table>

| **n-heptane** | 1) liquid-solid state $\sim$ 1.5 GPa. | 1) liquid-solid $\sim$ 1.2-1.5 GPa |
|              | 2) solid-solid $\sim$ 7.5 GPa$^{19}$ | 2) solid-solid transition $\sim$ 3 GPa$^{35}$ |
|              | 1) Above 10 kbar, with increasing pressure, significant changes occur in the environment around the CH$_3$ group rather than around the CH$_2$ groups. The same tendency of mode change like it could be seen for all of the light alkanes – with the liquid-solid transition all of the peaks become sharper, more intense and distinguishable. | 2) Definitive conversion of gauche to trans conformation in the solid phase. Disappearance of 197 cm$^{-1}$ (lattice mode). Disappearance of 278 and 295 cm$^{-1}$ methyl torsional modes. Disappearance of 367, 399, and 568 cm$^{-1}$ and the appearance of a new mode at 1144 cm$^{-1}$. An increase in intensity of the 1148 cm$^{-1}$ mode with a decrease in intensity of the 1090 cm$^{-1}$ mode. CH$_2$ and CH$_3$ stretching modes remain the same. |
SUPPLEMENTARY MATERIAL

See supplementary material for the decompression spectra both of n-butane and i-butane are in a good agreement with compression experiments, showing no strong difference in the vibrational character as well as phase behavior with the pressure change (figures S1 and S2). The complete vibrational assignment of the obtained modes was made in the “Results and discussion” section.

ACKNOWLEDGMENTS

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Paper C
Paper C

Raman Spectroscopy Study on Chemical Transformations of Propane at High Temperatures and High Pressures

DANIIL KUDRYAVTSEV, TIMOFEY FEDOTENKO, EGOR KOEMETS, SAIANA KHANDARKHAEVA, VLADIMIR KUTCHEROV, LEONID DUBROVINSKY

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Raman Spectroscopy Study on Chemical Transformations of Propane at High Temperatures and High Pressures

Daniil A. Kudryavtsev¹, Timofey M. Fedotenko², Egor G. Koemets², Saiana E. Khandarkhaeva², Vladimir G. Kutcherov¹,³ & Leonid S. Dubrovinsky²

This study is devoted to the detailed *in situ* Raman spectroscopy investigation of propane C₃H₈ in laser-heated diamond anvil cells in the range of pressures from 3 to 22 GPa and temperatures from 900 to 3000 K. We show that propane, while being exposed to particular thermobaric conditions, could react, leading to the formation of hydrocarbons, both saturated and unsaturated as well as soot. Our results suggest that propane could be a precursor of heavy hydrocarbons and will produce more than just sooty material when subjected to extreme conditions. These results could clarify the issue of the presence of heavy hydrocarbons in the Earth’s upper mantle.

Thermal and catalytic transformations of various hydrocarbon compounds at normal pressure have attracted significant attention in the field of petrochemistry. However, high-pressure chemistry of hydrocarbons as a science started to develop only recently,—primarily due to the unavailability of the specific equipment for the experiments. To date, only methane, the first member of the alkane homologous series, has been investigated when subjected to a wide range of pressures and temperatures⁴⁻⁵, because of its widespread occurrence in geological systems and well-known role in the atmosphere of the Solar System’s outer planets⁶⁻⁷. The behavior of other hydrocarbons, both unsaturated¹⁰⁻¹¹ and saturated¹²⁻¹³, have been less widely investigated with the use of various high-pressure techniques.

The focus on the significance of methane’s high-pressure high-temperature behavior implies that the fate of higher hydrocarbons has been ignored. Though the high-pressure, high-temperature (HPHT) behavior of ethane has been investigated several times¹²⁻¹⁴, propane has only been studied at ambient temperatures¹⁵⁻¹⁶. Propane is the third most abundant hydrocarbon on Earth after methane and ethane. It has been detected in the atmosphere of outer planets¹⁷ and their satellites¹⁸, and is a typical product of HPHT hydrocarbon synthesis performed both for chemical and geological purposes¹⁹⁻²⁰. The relevance of the investigation of carbon-bearing compounds can be understood from the perspective of the growing evidence of the role of hydrocarbon compounds deep in the Earth’s interior, which could contribute to the global carbon cycle²¹⁻²². Unfortunately, even for methane, investigations into its behavior under conditions of high pressure have yielded inconclusive and mutually conflicting results.

Propane’s importance as a petrochemical feedstock led to detailed studies of its thermal transformations in the range of 500–900 °C in processes such as pyrolysis and thermal cracking²³⁻²⁵. By changing the basic conditions of the process, the content of hydrocarbon compounds complex systems could be varied from higher normal and isoalkanes, dienes, aranes, and alkenes to C₁⁻C₃ fractions. These thermal processes were only investigated in the diapason under relatively mild pressures because of the process goal—low pressures are favorable for the synthesis of low-molecular compounds, while higher pressures could cause secondary reactions, particularly, polymerization and condensation, to occur²³.

Considering the previous information, this study deals with the HPHT study of propane under a pressure range of 2–22 GPa and a temperature range of ~900–3000 K.

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Methods
Propane (Linde Gas Polska), with a purity of 99.99%, was used in the experimental procedure without any additional purification. In our experiment, propane was subjected to cooling by liquid nitrogen and subsequent cryogenic loading in symmetric BX-90-type diamond anvil cells (DACs) equipped with synthetic, CVD-type IIa diamonds with a culet size of 250 μm. The rhenium gaskets were indented to a thickness of 25 μm. Pressure chambers with a step (Fig. S1 in supplementary) were prepared in the gaskets by combination of laser ablation and drilling. Thin (~1–2 μm) gold foil act as heat absorber in experiments with laser heating.

The Raman spectra were excited using a He-Ne laser (632.8 nm excitation). Then the acquisition of the spectra was made via the use of a LabRam spectrometer with a 2 cm⁻¹ spectral resolution. If possible, the pressure was determined by a calibration of propane high-pressure behavior, or else the pressure was determined by the first-order peak of the diamond. The uncertainties in the Raman peak positions were ±1 cm⁻¹. Raman spectra were collected at several points of the heating areas to ensure that the transformations being investigated, actually occurred. The Raman spectra of propane and the products of the reaction were measured before and after heating under the required thermobaric conditions.

In some cases, the green Ar⁺-laser (514.5 nm) the LabRam spectrometer (2 cm⁻¹ spectral resolution) was equipped with was also employed for the in situ analysis. The laser heating of the samples was performed using a home-laboratory laser heating setup at the Bayreuth Geoinstitut. This system could be described as traversable double-sided laser heating setup for diamond-anvil cells with the possibility of in situ temperature determination and precise heating of the samples inside a cell. Using high magnification and low working distance infinity corrected laser focusing objectives provided the opportunity of the laser beam size decrease less than 5 μm as well as achievement of the 320 times optical magnification.

Heating of the sample is carried out by two YAG lasers (1064 nm central wavelength). For temperature measurements the thermal emission spectra of the heated area is guided into an IsoPlane SCT 320 spectrometer with a 1024 × 256 PI-MAX 4 camera. The temperature was determined by fitting the black body radiation spectra of the heated area in a given wavelength range (570–830 nm) to the Plank radiation function. Liquid and solid propane are optically transparent and do not absorb well at the central wavelength of the YAG laser. This means that it is important to find a way to heat the sample and eliminate the catalytic influence of the absorber that could appear because of the usage of noble metals such as Ir. For these reasons, gold foil was employed as the absorber of the laser radiation to dissipate heat to the sample. The Raman spectra were measured at the hot points, near the hot points (marked as “near” on the several spectra), as well in the cold sample areas to facilitate a deeper understanding of propane’s behavior.

Results and Discussion
3GPa. The main chemical transformation of propane at 3 GPa (Fig. 1) observed at the temperatures displayed by Fig. 1 is a reaction with the prevalent formation of a sooty material. This material has very similar Raman spectra to the typical black solid compound obtained during the thermal and catalytic petrochemical processes or as a by-product of combustion according to the reaction:

**Figure 1.** Chemical transformations of propane at 3 GPa and T = 900–2300 K (±100 K). The reference peaks for graphite (soot) modes were taken from25,26, for C-H valence of hydrocarbon compounds2–4,12. The propane remained stable at 900 K. The spectra of untouched propane are in good correspondence with the previous experiments we carried out.27
During such processes, there is also the possibility of obtaining a graphite, which could be either disordered or highly ordered. However, the character of the presented spectra of the propane reaction products indicates the presence of disordered phases of graphite or soot. The highly ordered Raman spectra of graphite exhibits only one band (first-order G-bands) at 1580 cm\(^{-1}\) at ambient temperature. On the contrary, the disordered structure of graphite has the presence of additional first-order bands (D-bands) at 1360 and 1620 cm\(^{-1}\) depending on the ambient conditions. The bands in the region of 2800–3500 cm\(^{-1}\) could also correspond to the combinational models of D and G-bands. The signals of the graphite and soot are hard to distinguish, however, there is evidence that the soot itself has broader peaks. The spectra of propane under pressure of 3 GPa and at an ambient temperature of 900 K (±100 K) show no major changes in the display of any of the bands that are typical for propane. The stability of propane at a temperature of ~900 K is in good correspondence with the earlier experiments of Kolesnikov et al. on methane and ethane, showing the same behavior of propane. The absence of the hydrogen peaks in the region of 500–800 cm\(^{-1}\) (the region was not shown on the graph) can be explained as being due to the high rate of hydrogen diffusion through the rhenium gasket or through the reaction products. The appearance of the intense peak at ~3000 cm\(^{-1}\) at temperatures of 1420 and 1500 K (±100 K) could be attributed to C-H vibrations of various aliphatic hydrocarbons due to the well-known radical reaction mechanism resulting in the formation of methyl and ethyl radicals. These radicals could subsequently react via various pathways leading to the formation of hydrocarbon compounds:

\[
\text{C}_3\text{H}_8 = 3\text{C} + 4\text{H}_2
\]

Above mentioned reaction pathway may also explain why we do not observe pure hydrogen in the system. Hydrogen could be consumed in the reactions with other hydrocarbons:

\[
\text{C}_3\text{H}_4 + 2\text{H}_2 = 3\text{CH}_4
\]

**6GPa.** Heating at 940 K does not affect Raman spectra of propane (Fig. 2).
The spectra collected after heating at higher temperatures characterized by presence of bands at ~3100–3200 cm\(^{-1}\) (may be attributed to formation of unsaturated compounds\(^2\textendash}^4,\textendash}^12\)), and peak at ~3000 cm\(^{-1}\) (probably due to saturated hydrocarbon(s)). It is impossible to attribute these peaks to an individual compound or group of compounds due to high fluorescence in C-C stretching region or due to formation of ultradisperse diamonds\(^3\textendash}^\textendash}^30\). We hypothesize that due to complicated thermal mechanisms of propane transformations the products of polymerization or aromatization were obtained, for instance, via allyl-radical reaction:

\[
\begin{align*}
\text{CH}_3\text{-CH}_2\text{-CH}_3 & \quad \rightarrow \quad \text{CH}_2=\text{CH}\text{-CH}_3 + \text{H}_2 \\
\text{CH}_2=\text{CH}\text{-CH}_3 + \cdot\text{CH}_3 & \quad \rightarrow \quad \text{CH}_2=\text{CH}\cdot\text{-CH}_2 + \text{CH}_4 \\
\text{CH}_2=\text{C}=\text{CH}_2 + \cdot\text{CH}_3 & \quad \rightarrow \quad \text{CH}_2=\text{C}=\text{CH} + \text{CH}_4 \\
2\text{CH}_2=\text{C}=\text{CH} & \quad \rightarrow \quad \text{polycondensation} \\
\end{align*}
\]

It is important to notice, that in the works of Kolesnikov et al.\(^3\textendash}^\textendash}^32\) the formation of unsaturated hydrocarbons wasn’t reported. Propane is heavier than methane by mass, and thus propane can easier decompose and produce larger number of hydrocarbon compounds.
8GPa. With the increase of the pressure to 8 GPa only methane could be identified among all of the hydrocarbons along with the formation of complex compounds with hydrogen at 1230 K (Fig. 3). These are formed due to the escape of hydrogen from the reacting system and the consequent formation of Van Der Waals bonds.

Unfortunately, the region of the hydrocarbon footprint lacks the characteristic peaks overlapped by the fluorescence. However, the C-H of aliphatic and unsaturated fragments in the region of valence vibrations suggests the presence of various hydrocarbon compounds. With the increase of the temperature up to 2000 K and higher, the formation of graphite-like systems could be seen with the total disappearance of C-H and C-C vibrations at 2350 K.
Another possible mechanism of hydrocarbon generation as well as hydrogen could be the interaction of various forms of carbon and hydrocarbons. There is evidence that C-H fluids could be in contact with carbon in the Earth’s mantle, which could lead to certain chemical reactions of hydrogenation. For example, the hydrogen generation in our case could be explained not only by thermal decomposition of hydrocarbons, but by the catalytic effect of the carbon in the form of graphite or soot.

11 and 14 GPa. The reference peaks for C-H valence of saturated hydrocarbon compounds were obtained from, for unsaturated hydrocarbons from, for graphite (soot) modes, they were obtained from, for propane from, for n-butane from, for n-pentane from, and for n-hexane from. The propane remained stable at temperatures of 840 K and lower. The spectra of untouched propane are in good correspondence with the previous experiments we carried out.

The formation of C1–C6 hydrocarbons at 11 and 14 GPa (Figs. 4 and 5 respectively) starting from 900 K corresponds with the previous results for methane of Kolesnikov and is in good agreement with the results from simulation experiments. The spectra of 11 and 14 GPa have a main, obvious difference—the presence of hydrogen. The absence of hydrogen at 11 GPa is because of hydrogen diffusion or secondary reactions of hydrocarbons or graphite. The C-C vibrations of n-butane, n-hexane, and n-pentane were detected in the spectra. In the case of the n-pentane and n-hexane, they were never detected in such types of experiments. This result proposes the complicated condensation mechanism that has a radical character, as in the case of industrial processes of pyrolysis. These series of reactions could be described with a classic radical-polymerization mechanism, because...
<table>
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<th>Pressure</th>
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<tr>
<td>3 GPa</td>
<td>298</td>
<td>C,H₆</td>
</tr>
<tr>
<td></td>
<td>900</td>
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<td>1230</td>
<td>C</td>
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<td></td>
<td>2311</td>
<td>C</td>
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<tr>
<td>6 GPa</td>
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<td>C,H₆</td>
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<tr>
<td></td>
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<td></td>
<td>1200</td>
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<td>1500</td>
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<td>8 GPa</td>
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Table 1. Overview of the experiments carried out during the investigation.
of a certain regularity in the decreasing intensity of the hydrocarbon peaks with the consequent increase in the molecular mass. By modifying the reaction of \( \text{CH}_4 \rightarrow \text{C}_6 \text{H}_6 + \text{C}_6 \text{H}_2 \text{O} + \text{C}_6 \text{H}_{10} + \text{C}_6 \text{H}_{12} + \text{C}_6 \text{H}_{14} \ldots + \text{H}_2 \)

The most important fact that was observed during the experiments at 14 GPa is the contemporaneous presence of hydrogen, graphite, and other hydrocarbons during the laser heating, which could be interpreted as the equilibrium state. However, with the pressure increase it is hard to distinguish the particular hydrocarbon signal. After 1500 K only graphite and C-H valence vibrations could be seen.

### 17 GPa and 22 GPa

At 17 and 22 GPa the Raman bands of hydrocarbons become less distinguished with the overlap of the C-C bending region by graphite frequencies with the presence of unidentified C-H vibrations of saturated hydrocarbons in the region of 3000 cm\(^{-1}\) (Figs. 6 and 7).

### Summary of The Results

The Table 1 and Fig. 8 summarize observations described above. Our experiments demonstrate that at pressure and temperature conditions relevant for wide range of depth within the Earth pure propane (without any catalyst) can transform in to different hydrocarbons, both saturated and unsaturated. Under these conditions propane is reacting via two simultaneous and competing pathways – (1) the growing of the hydrocarbon chain via condensation or polymerization mechanisms with the formation of higher hydrocarbons and (2) destruction via the cleavage of C-C and C-H bonds with the formation of lighter hydrocarbons and also graphite (or sooty material). Our observations suggest that propane, if subducted in to the mantle, undergoes complex transformations and may be source of more complex organic compounds. The issue of presence of heavy hydrocarbon compounds in the Earth’s mantle was thoroughly described and examined in these works.

### Conclusion

The observations of propane chemical transformations under a wide range of high pressures and temperatures that are also present in the Earth’s mantle and in subduction environments, provides an insight into the fate of the carbon-bearing fluids fate deep in the Earth’s interior. The thermodynamic stability of propane under the pressures of 3–14 GPa and temperatures less than 900 K have been shown. At temperatures greater than 900 K, over a full range of pressures, propane transformation led to the formation of complex hydrocarbon systems and soot. At pressures of 11 and 14 GPa it was possible to identify the product mixture which includes light hydrocarbons, methane, and ethane and heavy hydrocarbons such as n-butane, n-pentane, and n-hexane.

We also have shown that the formation of heavier alkanes from propane at temperatures in the range of ~1000–2000 K and under pressures from 6 to 22 GPa is possible without any catalysts, and corresponds to the reactions leading to the formations of similar compounds occurring at depths of more than 130 km beneath the Earth’s surface.

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Author contributions
D.K., K.V. and L.D. designed the experiments. K.V. provided the idea of study. D.K., L.D., S.K., E.K. and T.F. participated in the conducting of the experiments. D.K. and S.K. did all of the preparations for the high-pressure experiments. T.F. and D.K. did the laser heating of the sample. E.K. and D.K. performed the cryogenic loading of propane. Collection and analysis of Raman spectra were made by D.K. D.K. wrote the text of the paper with essential advices from L.D. All authors reviewed the manuscript.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary information is available for this paper at https://doi.org/10.1038/s41598-020-58520-7.

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Paper D

High-pressure chemistry of propane

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Minerals
High-pressure chemistry of propane
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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 μm. For the high-pressure study at ambient temperature, the rhenium gasket was indented to a thickness of 35 μm where the hole of 110 μm 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 μm and 80 μm 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 μm) 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 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 ~3-5 μm 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 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 ±1 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 \( \approx 870 \text{ cm}^{-1}/1057 \text{ cm}^{-1} \) in the case of propane;
b) CH\(_3\) and CH\(_2\) bending modes 1400-1500 cm\(^{-1}\);
c) Methyl (CH\(_3\)) and methylene (CH\(_2\)) stretching modes 2800-3200 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.
Figure 2. Raman spectra of propane (C₃H₈) collected at high pressure with constant ambient temperature ranging from 5.1 (5) to 40.0 (5) GPa. Three phase transitions were identified in the range of interest – at 6.5 (5) GPa, 14.5 (5) GPa and 26.5 (5) GPa. The pressure points between identified phase transitions are showed in this work [36]. The approximately same phase transitions could be seen at the decompression spectra. The hysteresis value does not exceed the error in the pressure measurement using the ruby luminescence line (±0.5 GPa).
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 cm\(^{-1}\), where some of the hydrocarbon’s bands are presented. The second-order diamond peak at 2100-2700 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 cm\(^{-1}\) quite tricky even at high resolutions. In the case of IR spectroscopy, the region of 1800-2650 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](image_url)

Figure 3. Chemical transformations of propane at 11 GPa and T = 840-2420 K (±100 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:

\[
\begin{align*}
\text{CH}_4 \rightarrow C_2H_6 + C_3H_8 + C_4H_{10} + C_5H_{12} + C_6H_{14} \ldots + H_2
\end{align*}
\]

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 $T = 930$-$1580$ K ($\pm 100$ 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 Podsiadlo 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\textsubscript{3}H\textsubscript{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.
References

Figure A1. Chemical transformations of propane at 3 GPa and T = 900-2311 K (±100 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 $T = 940$-$1600$ K ($\pm 100$ 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 \( T = 893-2500 \) K (±100 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 \( T = 920-3100 \) K (±100 K).
Figure A5. Chemical transformations of propane at 22 GPa and T = 930-2130 K (±100 K).