Observing Phase Changes in n-hexane from 0 to 12 GPa

Abhishek Terala, Aniya Means, Kevin Vencatasamy

University of Rochester

Funded by the Center for Matter at Atomic Pressures (CMAP), an NSF Physics Frontier Center

Abstract

Diamond Anvil Cells and Raman Spectroscopy have been used in unison to explore the relationship between bond behavior and pressure. Understanding how bonds behave under certain extreme conditions can help better understand the atmospheres of other planets and aid in modeling them. Our project focused on studying n-hexane, a straight-chain hydrocarbon present in Jupiter's atmosphere. Using a shock DAC, the behavior of n-hexane from pressures of 0 to 12 GPa was analyzed. Diamonds with 700µm culet size were surrounded by a stainless steel gasket with an imprint thickness of 121µm. A gearbox was used to evenly increase the pressure by tightening four pressure screws. Raman Spectroscopy and images were taken at incremental pressures and analyzed to look for possible changes in bond structure. The results showed that n-hexane exhibited a phase change at approximately 2.1 GPa, aligning with the current published literature. Further experiments could involve using x-ray crystallography and changing the temperature of the cell to expand the phase diagram and thereby aid in fuel storage and understanding the state of hydrocarbons, water, and ammonia in gas giants' atmospheres.

Methods

Raman Spectroscopy:

Raman Spectroscopy is a technique used to analyze the nature of bonds between molecules within materials. Molecules are excited using a monochromatic light source, raising their energy state. As the molecules relax back to their ground state, light is emitted. The spectra of the emitted light are analyzed to understand the behavior of intramolecular bonds. Raman Spectroscopy can result in three different types of scattering: Rayleigh Scattering, Stokes, and Anti-Stokes (Figure 1), from most to least common.

Diamond Anvil Cell:

Diamond Anvil Cell (DACs) were first used in 1958– the DAC has been the most effective way to reach extremely high pressures using both static and dynamic compression. Utilizing the hardness of a diamond and a fine culet, the pressure inside a chamber sealed with a gasket can be raised up to 550 GPa statically. The diamonds used are Type 1AS (flawless) with ultra-low fluorescence to minimize peaks on the spectra caused by the diamond. Types of DACs include Static and Shock. In this experiment, a Shock DAC was statically loaded.

Setup

Cleaning:
- DACs were cleaned using isopropanol.
- 4000 grit sandpaper was used to remove any residue from previous use.

Alignment:
- Culets were aligned using a microscope.
- A stainless steel gasket blank was cleaned and placed between both diamonds. The cell was then closed and tightened.

Sealing:
- Four pressure screws were tightened incrementally to ensure the gasket created a perfect seal around both diamonds.
- The thickness of the gasket was measured using a pointed micrometer and adjusted until dimensions were up to standard.
- The gasket was then drilled using EDM (Electric Discharge Machining), creating a chamber for the sample to be placed in.

Loading the Sample:
- The sample was placed between both diamonds, surrounded by the gasket.
- Using pressure screws, the cell was brought closer together, increasing pressure in the chamber.
- Screws were tightened using a gearbox to prevent uneven pressures.

Data Collection:
- A class 3B 532 nm laser was used to excite molecules.
- Raman Spectroscopy and images were taken at various pressures ranging from 0 to 12 GPa. Pressure was measured using Ruby fluorescence.

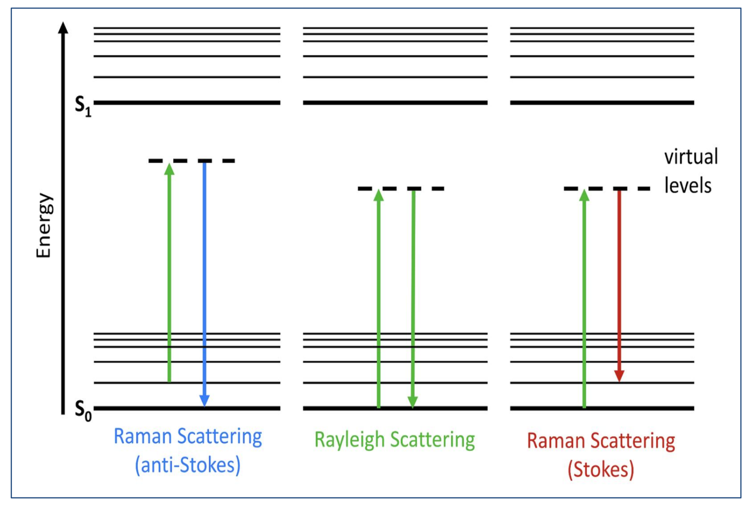

Figure 1. Visualization of the Behavior of molecules analyzed under Raman Spectroscopy

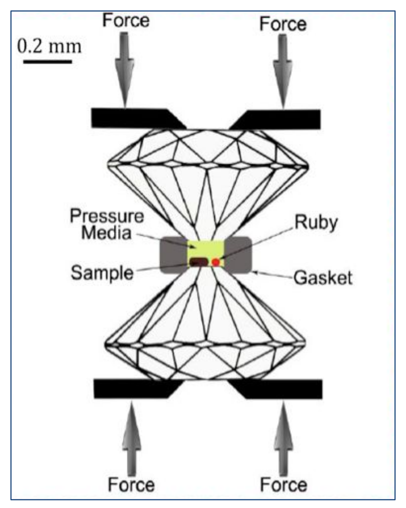

Figure 2. Cross Section of the Experimental Region of a DAC

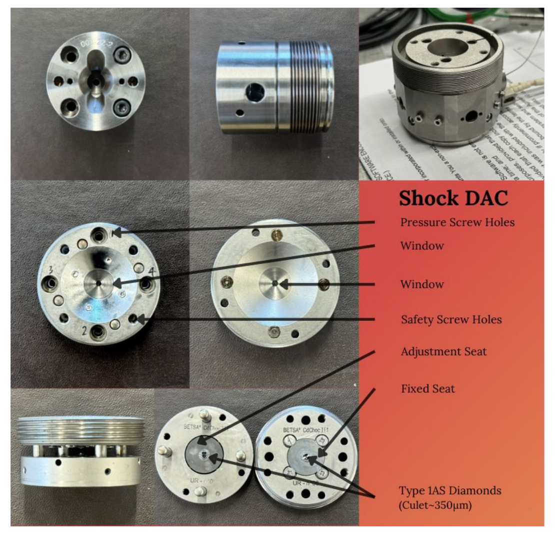

Figure 3. Different types and Components of a DAC

Sample Preparation

- Clean all faces of the DAC and the gasket using Isopropanol
- Use 4000 grit sandpaper to scrape off any residue on the DAC from previous use
- Lubricate the pins and holes using lithium grease to minimize friction while closing the cell
- Close the cell and bring both culets close together; use a safety screw to ensure the diamonds do not collide
  - Align them using the adjustable seat and Allen keys
  - A microscope was used to ensure precision
- Once the faces are aligned, open the cell and place the gasket blank on top of one of the diamonds
  - Center the blank
  - Use clay for balance
  - Mark north for replication
- Close the cell and slowly tighten the pressure screws in a cross pattern
- Open the cell and measure the thickness of the gasket
  - The process yielded a gasket with a thickness of 121 µm
- Use an Electric Discharge Machining (EDM) tool with a 400µm bit to drill through the gasket
- Place the gasket in the cell, resting on a diamond
  - Place a small ruby crystal in the chamber as a pressure medium
  - Use a microneedle to load the n-hexane
- Close the cell and begin compressing

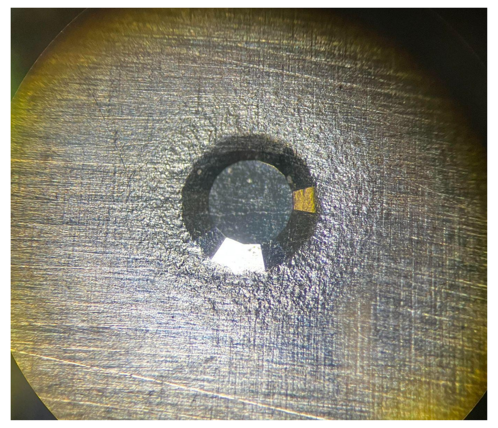

Figure 4. 121 µm Indented Gasket.

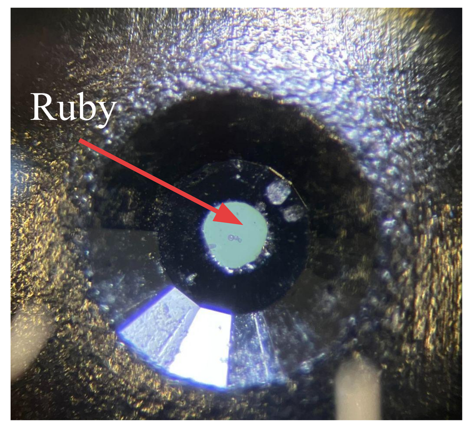

Figure 5. Pressure medium (Ruby) in Gasket Chamber.

Results & Analysis

Pressure readings in the chamber were found using a Ruby as a pressure medium. The spectra from 0.17 to 11.89 GPa are overlaid in Figure 6. There is a visible change in the spectra throughout the pressure range. These results are indicative of a change in bond nature within the sample.

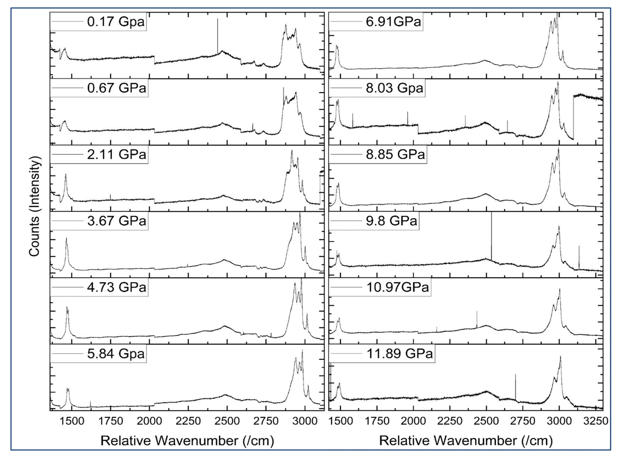

Figure 6. Overlay of Spectra taken from 0.17 to 11.89 GPa.

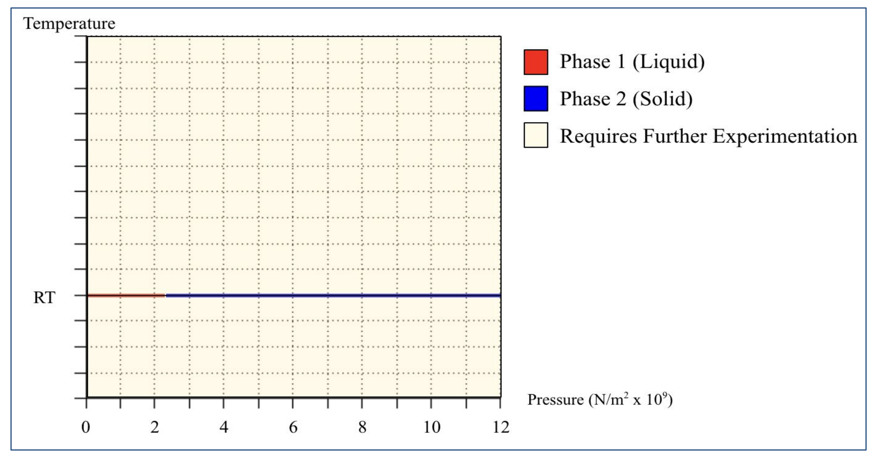

Figure 7. Recorded Phase Diagram of n-hexane (Incomplete).

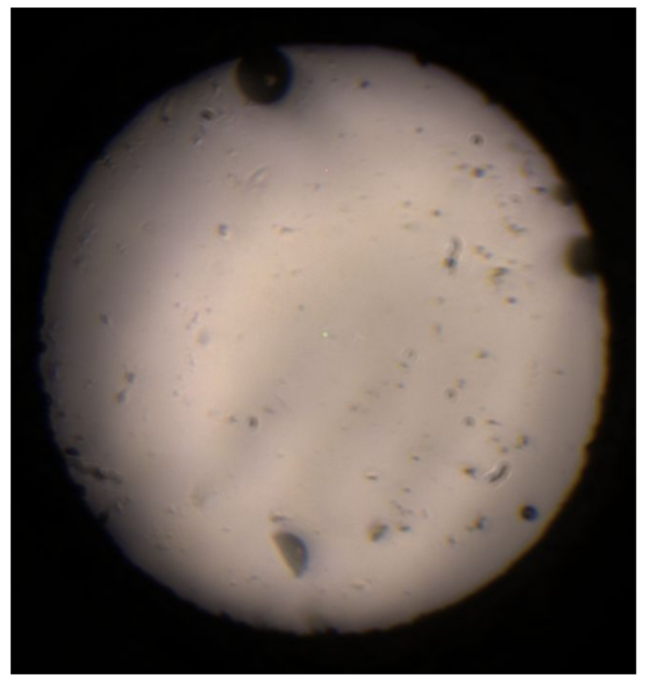

Figure 8. Image of n-hexane at 0.17 GPa (Liquid)

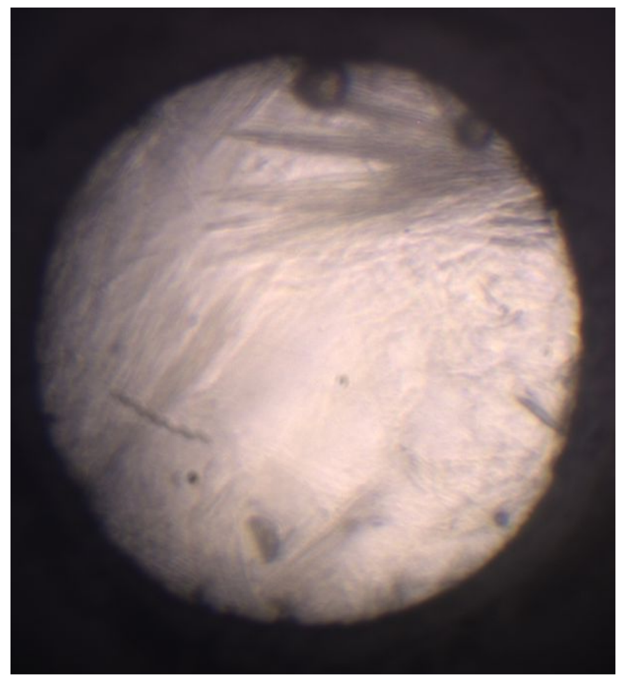

Figure 9. Image of n-hexane at 2.11 GPa (Solid)

Discussion

- The sample turns into a solid at 2.11 GPa.
  - This is supported by Figure 8 and 9 which shows new textures at 2.11 GPa.
  - Another piece of evidence is that at this pressure, a sharp peak appears at 1400 cm^{-1} indicating a change in phase structure.
  - There are two possible reasons regarding the formation of this peak:
    - The bond structure was slightly altered resulting in a stronger emission.
    - As the pressure increases the amount of molecules per unit volume is increasing. This leads to more molecules being excited and emitting more light of that wavenumber.
- As pressure increases past 2.11 GPa, the sharp peak at 1400 cm^{-1} splits into a duplet.
- Before 6.91 GPa, the first peak of the duplet is larger than the second one.
  - The intensity of the first and second peaks reverse at pressures beyond 8.03 GPa, indicating a possible new solid structure.
- The multiplet at 2900 cm^{-1} changes in shape as the sample transitions from liquid to solid.
  - Turns into a triplet and then a duplet with a "tail" from 6.91 to 11.89 GPa
- These are indications that while the sample is still solid, its bond structure is rearranging.

Conclusion

Although it was found that n-hexane solidifies at 2.11 GPa at room temperature, this may change at different pressures. To expand its phase diagram (Figure 7), it is necessary to carry out experiments at different temperatures and pressures, aiding in better understanding the behavior of the molecule in varying environmental conditions. By carrying out these further experiments, the melting line of n-hexane can be plotted out more extensively. This can be achieved using the heater diamond anvil cell (Figure 3).

Using x-ray crystallography at each subsequent pressure point, the molecular arrangement of the material can be tracked to observe for changes in lattice structure. By looking for the various ways the molecules of n-hexane arrange themselves at various pressures and temperatures, the phase diagram can be further expanded. This also has implications in fuel storage, and the study of clathrate cages (Figure 10). If a lattice structure is able to form a clathrate, other smaller molecules, such as hydrogen and ammonia, can be stored within the space aiding in transport and use of highly reactive compounds.

Since a DAC represents a microcosm of the atmosphere of gas giants, expanding the phase diagram can further the understanding of the behavior of these hydrocarbons on gas giants such as Jupiter and Saturn (Figure 11). The atmospheres of these plants greatly vary in temperatures and pressures based on the distance from the core (Figure 11). An expanded phase diagram of n-hexane can aid in understanding the behavior of these molecules throughout the atmospheres of these planets and improving their geophysical models.

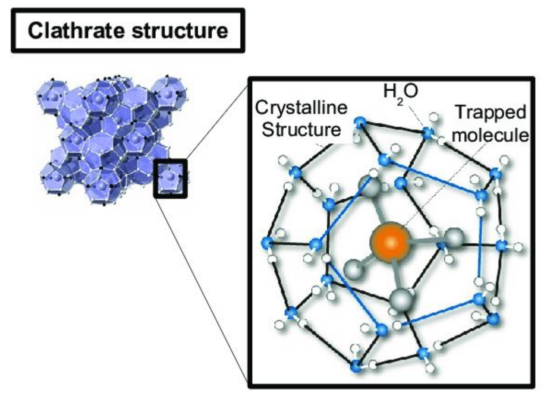

Figure 10. Visualization of a Clathrate

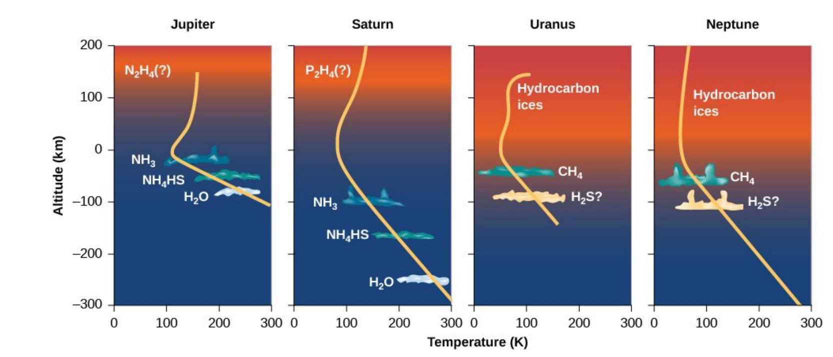

Figure 11. Breakdown of the known atmosphere of Gas Giants

References

[1] *X-ray crystallography: Revealing our molecular world | Science Museum*. (n.d.). Science Museum. https://www.sciencemuseum.org.uk/objects-and-stories/chemistry/x-ray-crystallography-revealing-our-molecular-world#:~:text=X%2Dray%20crystallography%20is%20a,called%20an%20x%2Dray%20camera.
[2] Edinburgh Instruments, Blog: What is Raman Spectroscopy?
[3] Wikipedia contributors. "Diamond anvil cell." Wikipedia, The Free Encyclopedia. Wikipedia, The Free Encyclopedia, 24 May. 2024. Web. 30 Jul. 2024.
[4] Daniel, H. (2016, March 23). *What the Heck is a Diamond Anvil Cell?* DCOECS15 OPEN SCIENCE BLOG. https://dcoecs15.wordpress.com/2016/03/23/what-the-heck-is-a-diamond-anvil-cell/
[5] Weir, C. E., Van Valkenburg, A., Lippincott, E. R., Bunting, E. N., Mineral Products Division, University of Maryland, NBS laboratories, General Services Administration, NIST Museum, Wachtman, J. (Jack) B., Block, S., Barnett, D., Piermarini, G., Forman, R., Parker, H. S., & Brower, W. S. (n.d.). *The Diamond Anvil pressure cell*. https://nvlpubs.nist.gov/nistpubs/sp958-lide/100-103.pdf
[6] Marboeuf, Ulysse. (2011). A model of cometary nucleus taking into account all phase changes of water ice: amorphous, crystalline, and clathrate.
[7] OpenStax. (n.d.). 11.3 Atmospheres of the Giant Planets. Pressbooks. https://pressbooks.online.ucf.edu/astronomybc/chapter/11-3-atmospheres-of-the-giant-planets/