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What rocks on Titan? New phases of acrylonitrile and prospects for mineralogy with organic molecules

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Abstract

We have undertaken a number of experimental investigations to explore the minerals on Saturn's moon Titan. Specifically, for this contribution we wish to report the results we have recently obtained for solid acrylonitrile, where we have discovered a hitherto unknown phase that would be stable under Titan conditions.

1. Introduction

The Cassini-Huygens mission revealed Saturn's largest moon Titan to be a diverse world, with geological features that are astonishingly similar to those found on our own world. With vast seas and lakes, sweeping dunes of organic sands and dissected plateaus, the evidence is mounting that the landscape of Titan has been shaped by both fluvial and eolian processes. However, there are stark differences between Earth and Titan, such as the temperatures and materials that shape their respective landscapes. Over the last few years our collaboration has worked to understand the materials that would form and shape the landscape on Titan. This has revealed the lack of even basic crystal structural information for many of the molecules that are proposed to exist on the surface. Hence, we are working to rectify this, using a variety of laboratory techniques [1].

Of the molecules predicted to be formed by Titan photochemistry, acrylonitrile (CH_2CHCN, also known as 2-propenenitrile and vinyl cyanide) has garnered interest of late having recently been observed in the atmosphere of Titan [2]. Additionally, based on theoretical modelling, acrylonitrile has been hypothesized to be able to form membrane-like structures in liquid methane [3], providing the potential for non-aqueous biological functions.

However, despite the intense interest that acrylonitrile has received from the planetary science community, it has been rather unexplored by crystallography and diffraction experiments. Liquid at room temperature, acrylonitrile freezes at ~190 K with spectroscopic results suggesting that it undergoes a phase transformation at 160 K [4]. The Cambridge structural database only contains one entry for pure acrylonitrile (refcode POQMIR represented in Figure 1), a disordered orthorhombic phase determined at 153 K from a single crystal X-ray diffraction study [5].

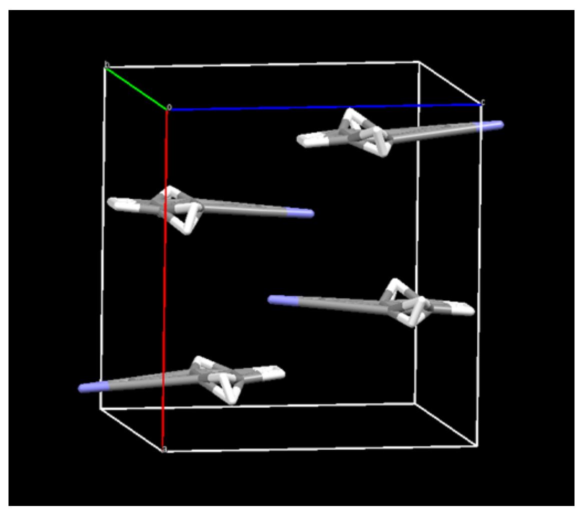

Figure 1: The only known crystal structure of acrylonitrile prior to this study, determined at 153 K. The molecule is disordered, and hence likely to undergo a phase transition at lower temperatures.

2. Experimental

We have examined the crystal structure of acrylonitrile at temperatures between 80 and 170 K with powder x-ray diffraction, neutron diffraction as well as Raman spectroscopy. For the diffraction experiments, liquid acrylonitrile ($\geqslant$99%, contains

35-45 ppm monomethyl ether hydroquinone as inhibitor, Sigma Aldrich) was placed into either a glass capillary (for X-ray diffraction) or vanadium can (for neutron diffraction) before being cooled and crystallised. For each technique the sample was cooled to the base temperature (80 K for X-ray diffraction and 5 K for neutron) before diffraction data was collected at a range of intervals.

For the Raman spectroscopy, a drop of liquid acrylonitrile was placed into a liquid nitrogen-cooled cryostage (Linkam Scientific Instruments Ltd.) at 90 K. Raman spectra within the cryostage were obtained using a high-resolution confocal dispersive micro-Raman spectrometer (Horiba Jobin Yvon LabRam HR) equipped with a 50 mW Nd:YAG laser (frequency-doubled 532 nm) as the excitation source. Thermal stability studies were performed by warming in 5 or 10 K increments and obtaining Raman spectra following a 5-minute equilibration time.

3. Results

Initial analysis has shown that acrylonitrile does indeed undergo a phase transition to novel forms at low temperatures. This is particularly clear in the neutron diffraction data presented in Figure 2.

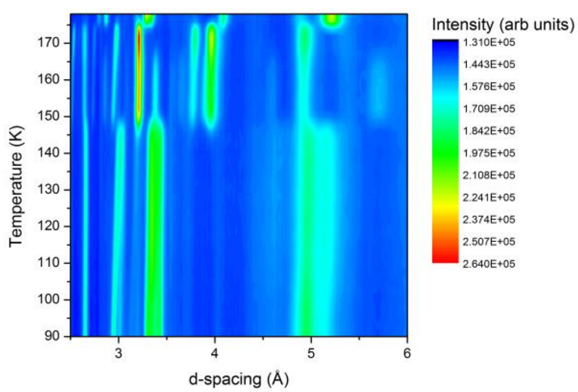

Figure 2: Thermodiffractogram of neutron diffraction data collected from acrylonitrile. It clearly shows three distinct phases, with phase transitions at 145 – 150 K, and 175 K. The highest temperature phase matches to the known phase discussed in the introduction.

Our X-ray and neutron diffraction data show that there are three distinct phases of acrylonitrile with temperature and we are currently undertaking structural analysis to determine first unit cell volumes (from which we will infer density) and also structural co-ordinates. Together with Raman spectroscopy, we hope to fully describe the changes in acrylonitrile structure with temperature. At present we believe that the changes are driven by the progressive ordering of the individual molecules.

4. Conclusions

As solid acrylonitrile is likely to be an important mineral upon the surface of Titan we have examined its crystal structure behaviour with temperature. We have found two new phases and hope to report the density and atomic co-ordinates of these shortly. The crystal structure of a solid material is one of its most fundamental properties, and is necessary for understanding intermolecular interactions and for prediction of mechanical and chemical properties – such as the ability to support deep valleys, high canyon walls, and resist erosion. Using Titan as a model, this work helps establish the framework for a new understanding of possible geological processes on cold hydrocarbon worlds.

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