NUCLEAR MAGNETIC RESONANCE (NMR) AS A TOOL FOR IN-SITU DYNAMIC ANALYSIS OF TITAN'S LAKES. F. Cary[1], E. Kelly[1], J. Hyvl[2], M. Malaska[3], K. Arroyo-Flores[1], A. McFall[1] and P. Englert[1]. [1]Hawaii Institute of Geophysics and Planetology, (fcary@hawaii.edu), [2]University of Hawaii Department of Chemistry, [3]Jet Propulsion Laboratory/California Institute of Technology.

Introduction: Saturn's moon Titan has a dynamic surface environment characterized by its thick organic-rich atmosphere, hydrocarbon 'hydrosphere', and cryogenic surface temperatures of 94 K [1]. Titan's chemical composition has been explored with gas chromatography mass spectrometry (GCMS) [2] and modeling [3], but the chemical processes occurring on Titan remain poorly understood. Elemental abundances obtainable through GCMS are not sufficient to answer questions relating to molecular structure and interactions in cryogenic chemical regimes, especially given weak intermolecular forces play a crucial role in chemical interactions at low temperatures [4]. It is necessary to reconsider previously deployed physicochemical analysis methods, and propose a non-destructive, highly informative instrument that can detect molecular structures in Titan's native environment and inform chemical processes occurring at the surface. We propose nuclear magnetic resonance (NMR) spectroscopy to be advantageous for Titan, and advocate for it as a novel approach to investigate the dynamic chemical environment of Titan lakes for potential incorporation in future mission planning and technology development for exploring the outer solar system.

Instrumentation: NMR has been proposed in the past as potentially useful for analyzing Titan environments [5][9] and has four key advantages that are applicable when investigating the chemistry of a Titan environment. 1) NMR spectra are highly informative, and can deduce information on the physical, chemical, and electronic properties of the sample molecules [6], including weak protein-protein intermolecular interactions in biological applications [7] and the identification of functional groups [8]. NMR can map interatomic distances and connectivity relationships between different atoms in chemical structures; a level of detail that warrants attention for application to complex mixtures in situ on Titan [9] and surpasses what is achievable by other instruments. This ability will be highly useful in understanding the structural evolution of molecules present in Titan liquids and how they interact. 2) ^{1}H and ^{13}C NMR techniques analyze structures containing ^{1}H and ^{13}C isotopes, and ^{13}C isotopes have a slightly higher abundance on Titan [2], increasing the usefulness of NMR on hydrocarbon worlds [10]. Additionally, at low temperatures, there are more nuclei in the ground state which would increase the sensitivity of NMR to compounds in this environment. 3) NMR operates at cryogenic temperatures. Whether a permanent or superconducting magnet is used, NMR would be able to analyze samples at ambient Titan temperatures, relative to other instruments that operate at warmer temperatures. 4) NMR is non-destructive to the samples collected in-situ, which is a key advantage because gentle analysis methods are critical to answer science questions relating to natural chemical processes occurring on Titan, and allows for analysis of chemical interactions in real time.

Our work utilizes a high field strength (400MHz) NMR with a superconducting magnet. However, using a superconducting magnet for space exploration has significant practical difficulties. Benchtop NMRs with permanent magnets are better suited for space exploration, but currently have low field strengths (~100 MHz). Developing benchtop NMRs to have higher field strengths is an active area of research [11] and could allow for a decrease in spatial dispersion and an increase in the viability of the NMR for our purposes and for future exploration of Titan.

Related Science Objectives: Future exploration seeking an understanding of physical chemistry on Titan will have the following questions to address: What are the molecules present in Titan's lakes? Are any of them more associated with each other than we would expect? How are molecules changing at the surface-atmosphere boundary? And, how could molecules interact and react in a native Titan environment? Our work investigates the utility of NMR for studying dynamic chemical interactions in other, non-aqueous, planetary liquids, and assesses the capabilities of NMR to provide more information than previous instrumentation methods for addressing these questions in future.

Experimental Application: To determine whether NMR produces the desired results in cryogenic hydrocarbon solutions, our proof of concept experiment uses analogue Titan chemicals combined in a variety of mixtures based on their expected concentrations in Titan lakes [2]. These are dissolved in deuterated hexane (d_{14}-C_6H_{14}) and prepared as appropriate for the initial physical phases of the reagents mixed: solid, liquid, and gas. The mixtures are cooled to a temperature range where they can be observed in a liquid state at 190 K using a 400 MHz

NMR for analysis. In these experiments, we measure the ^{1}H, ^{13}C, and 2-Dimensional $^{1}H/^{13}C$ chemical shifts of: propane (C_3H_8), butene (C_4H_8), butane (C_4H_{10}), anthracene ($C_{14}H_{10}$), naphthalene ($C_{10}H_8$), benzene (C_6H_6), hexane (C_6H_{14}), acetonitrile (C_2H_3N), acrylonitrile (C_3H_3N), and acetylene (C_2H_2), in analogous chemical and physical conditions to Titan's lakes. The results are analyzed to determine the chemicals present in the mixtures, their structure, as well as any interactions between them by locating chemical shifts.

Preliminary Results: NMR spectra were obtained that were able to detect chemical shifts associated with the structures of all individual compounds listed above, except acetonitrile and anthracene due to their immiscibility in hexane. Given this, we hypothesize that acetonitrile and anthracene would accumulate at the bottom of lakes on Titan. A spectrum obtained of acrylonitrile and hexane was able to distinguish between monomers and polymers of acrylonitrile, by observing broad chemical shifts in the 5.4 to 6.5 ppm range, which overlapped with the expected three chemical shifts from the monomeric acrylonitrile. Our results also inform the detectability of aromatic and alkane hydrocarbon compounds that have chemical shifts between 6-8.5 ppm and below 3 ppm, respectively, as they may appear to overlap on a lower field strength NMR spectrum, resulting in a failure to resolve them.

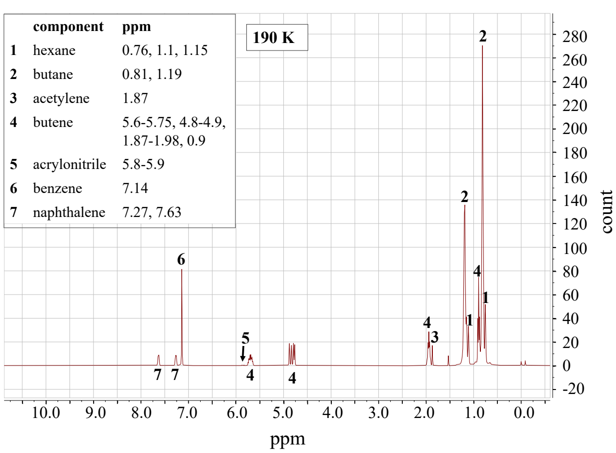

Figure 1: *^{1}H NMR spectra from sample containing d_{14}-C_6H_{14} (solvent), C_4H_8, C_4H_{10}, $C_{10}H_8$, C_6H_6, C_3H_3N, and C_2H_2 at 190 K, using TMS as an internal standard.*

Figure 1 displays a ^{1}H spectrum of a 7-component mixture, where the C_4H_8, C_4H_{10}, $C_{10}H_8$, C_6H_6, C_3H_3N, and C_2H_2 structures are distinguished by their individual chemical peaks. There is evidence for an acetylene chemical shift of 0.03 ppm, indicating a small degree of interaction with the other molecules. The results show that the prevalence of alkanes on Titan will likely complicate identification and require the use of additional techniques such as ^{13}C and 2D NMR, or more complex pulse sequences.

Expected Outcomes: These experiments establish that NMR can successfully deduce the chemical structures of hydrocarbon mixtures at Titan-like concentrations and conditions. This suggests that NMR could be a useful instrumentation technique for in situ non-destructive analysis on Titan. This work also informs future instrument development by advocating for a critical re-evaluation of present-day instruments to assess their usefulness at answering new science questions in increasingly unique environments.

Conclusion: NMR is highly useful for analyzing Titan analogue chemistry and could provide a unique insight into the molecular processes occurring on Titan. Incorporating NMR on future missions could establish a critical background in understanding cryogenic chemistry and chemical processes occurring in the surface liquids of Titan. Understanding the distribution of molecules and structural diversity in Titan liquids could help us understand if there is chemical evolution and cycling occurring in these environments, which are processes foundational for transitioning a chemical planetary environment to a living system as occurred on Earth [12]. This would assist in assessing the possibility of life in alternative chemical surface environments elsewhere.

Acknowledgments: We acknowledge the Hawaii Institute for Geophysics and Planetology (HIGP) for providing funding for materials, and the Hyvl Lab for hosting our experiments. We acknowledge Wesley Yoshida from the University of Hawaii Chemistry Department for assisting us in the acquisition and analysis of our NMR results.

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