UNDERSTANDING GEOCHEMISTRY ON TITAN'S SURFACE WITH MOLECULAR MODELING.
R. C. Remsing[1], A. C. Thakur[2], H. W. Longo[2], P. Chakraborty[2], O. Martin[2]. [1]Department of Chemistry and Chemical Biology, Rutgers University, Piscataway, NJ 08854, rick.remsing@rutgers.edu, [2]Department of Chemistry and Chemical Biology, Rutgers University, Piscataway, NJ 08854.

Introduction: The Saturnian moon Titan has a thick, organic rich atmosphere and a cold surface temperature of approximately 94 K. As a result, hydrocarbon lakes and seas are present on Titan's surface. In addition, Titan's surface is expected to be coated with crystalline solids composed of small organic molecules, called cryominerals. Consequently, geochemistry on Titan, as well as non-aqueous prebiotic chemistry, involves hydrocarbon liquids, cryominerals, or the interfaces where the liquids and cryominerals meet. To fully understand chemical processes in these unique environments, a molecular-level picture is needed, which we are working towards using computational molecular modeling. We have modeled chemical structure and dynamics in several cryominerals and found that many may exist in plastic crystal phases that are relevant to understanding chemical and mechanical properties of Titan's surface. We have also developed new models of liquid methane and ethane, which we use to study solvation, self-assembly, and model chemical reactions in Titan's seas and their interfaces. The result of this work has implications for modeling the properties of Titan's surface and understanding driving forces for prebiotic chemistry in Titan-like non-aqueous environments.

Titan's Plastic Cryominerals: We use first principles, quantum mechanics-based simulations to model co-crystals of small organic molecules that have been predicted to exist on the surface of Titan [1,2]. We find that, at Titan surface conditions, several of these cryominerals are in a plastic crystal phase, in which molecules are translationally ordered but rotationally disordered. For example, in the acetylene:ammonia (1:1) co-crystal, the ammonia molecules are orientationally disordered and rotate on picosecond timescales [3]. These rotational dynamics are sped up by nuclear quantum effects, which are important at low temperatures. The disorder present in plastic crystals generally impacts important thermodynamic and mechanical properties relevant to surface processes, such as reducing elastic moduli.

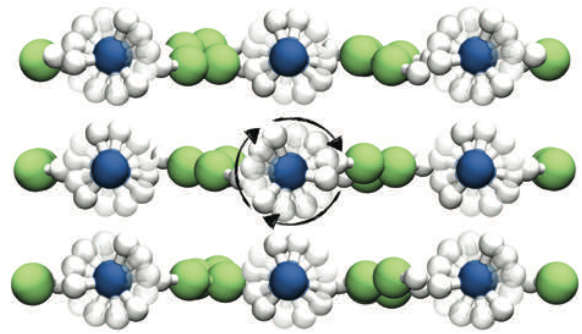

Figure 1. *Schematic illustration of orientational disorder and rotational motion of ammonia molecules within the acetylene:ammonia (1:1) plastic co-crystal. Carbon atoms are green, hydrogen atoms are white, and nitrogen atoms are blue.*

Self-Assembly at Hydrocarbon Interfaces: On Earth, water-mineral interfaces play important roles in geochemistry and prebiotic chemistry. In analogy, one may anticipate that liquid hydrocarbon-cryomineral interfaces could play similar important roles on Titan. To gain insights into these interfaces and their potential for facilitating chemical processes, we use computer simulations to investigate model interfaces between liquid methane-ethane solutions and simple solid surfaces. We use our recently developed models for methane and ethane to accurately describe solvation in these liquids [4]. For methane-ethane mixtures, we find that methane forms the outermost layer of the interface, at both liquid-vapor and liquid-solid interfaces. We are also exploring the adsorption and self-assembly of small molecules at solid surfaces. We find that HCN molecules adsorb to hydrogen-bonding surfaces and self-assemble into structures that may facilitate further reactions relevant to prebiotic chemistry, Figure 2.

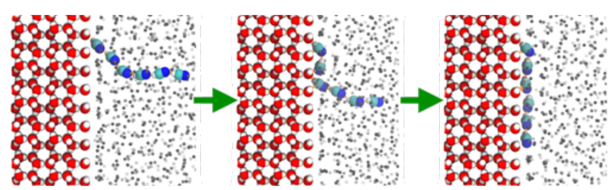

Figure 2. *Snapshots showing the adsorption of an HCN H-bonded polymer to the surface of ice Ih. The HCN at the end of the polymer first forms a H-bond with a water molecule on the surface, then subsequent HCN molecules H-bond with the surface until the HCN chain lies flat on the ice surface. Oxygen is red, hydrogen is white, nitrogen is blue, carbon is cyan, and methane is shown as small gray spheres.*

Quantum Tunneling in Titan's Seas: On the cold surface of Titan, thermally driven chemical reactions are unlikely to occur. Instead, reactions relevant to prebiotic chemistry and biology must occur through other pathways. We are investigating how simple chemical reactions might occur in Titan's seas through non-thermal pathways, specifically quantum tunneling, wherein quantum mechanical effects enable reactions to proceed by passing through high energy barriers instead of going over them. We are simulating model proton transfer reactions, where the proton of a donor molecule moves to an acceptor molecule. By comparing simulations using classical and quantum descriptions of the nuclei in the system, we show that nuclear quantum effects can effectively lower reaction barriers at low temperatures typical of Titan.

Acknowledgments: This work is supported by the National Aeronautics and Space Administration under grant number 80NSSC20K0609, issued through the NASA Exobiology Program. We acknowledge the Office of Advanced Research Computing (OARC) at Rutgers, The State University of New Jersey for providing access to the Amarel cluster and associated research computing resources that have contributed to the results reported here. This work used the Advanced Cyberinfrastructure Coordination Ecosystem: Services & Support (ACCESS), formerly Extreme Science and Engineering Discovery Environment (XSEDE) [?], which is supported by National Science Foundation grant number ACI-1548562. Specifically, this work used Stampede2 and Ranch at the Texas Advanced Computing Center through allocation TG- CHE210081.

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