

The Fate of Simple Organics on Titan's Surface. Xinting Yu¹, Yue Yu², Julia Garver³, Xi Zhang², ¹Department of Physics and Astronomy, the University of Texas at San Antonio, One UTSA Circle, San Antonio, TX 78249 (xinting.yu@utsa.edu). ²Department of Earth and Planetary Sciences, University of California Santa Cruz, 1156 High Street, Santa Cruz, CA 95064. ³Department of Physics, University of California Santa Cruz, 1156 High Street, Santa Cruz, CA 95064.

Introduction: Photochemistry in Titan's thick nitrogen (N₂)- methane (CH₄) atmosphere creates a myriad of organic molecules, with at least 18 gas-phase species detected to date (for a list of the detected species, see [1]). These species include simple hydrocarbons such as ethane (C₂H₆), acetylene (C₂H₂), benzene (C₆H₆), and simple nitriles such as hydrogen cyanide (HCN), propionitrile (C₂H₅CN). On the other hand, the simple organic molecules in Titan's atmosphere can further coagulate and react to form the complex refractory organic particles that constitute Titan's thick haze layers. After the simple and complex organics are formed, because they are heavier than the background N₂-CH₄ atmosphere, they would descend through Titan's atmosphere. During their descent, the unique pressure-temperature profile of Titan allows these various organic molecules to condense into liquids or ices, forming stratospheric clouds. These simple and complex organics would eventually fall onto the surface of Titan, landing on dry surfaces or on the lakes and seas of Titan.

NASA's Dragonfly mission, arriving in 2034, will be exploring Titan's surface material in the equatorial region, where dry surfaces dominate. Thus, it is important to summarize all possible candidate materials that could be deposited from the atmosphere and their associated phases when they landed on the surface.

Titan, as the only moon that has standing liquids on its surface, has smooth and almost rippleless lakes and seas. Cassini's RADAR instrument has observed smooth lake surfaces with a surface height variation of less than 3 mm [2-4]. [5] suggests the possibility of a floating layer of sedimented cloud or haze materials on Titan's lake surfaces to dampen the surface waves. Previous works have investigated the floatability of refractory hazes on Titan's lakes [5-7]. Due to the uncertainty of the densities of various laboratory-produced Titan's haze analogs, "tholins," which can be higher or lower than the density of the lake liquids [1], the hazes may float on or sink into Titan's lakes. If the actual haze particles have a lower density compared to the lake liquids, the haze particles will float on the lakes. While if they are denser compared to the lake liquids - because the haze particles can be completely wetted by the lake liquids [6, 7], they will sink into the lakes and form lakebed sediments. Nevertheless, cloud condensates could also nucleate and cover the haze particles before they make contact with the lakes. Thus,

cloud particles made of various simple organics could be candidates for dampening the surface waves. Thus, a floatability study between the clouds and the lake liquids on Titan is necessary to assess such cloud-lake interactions and sediment floatability on Titan.

Methods: The compiled phase change points and saturation vapor pressures of the detected gas-phase simple organics species in [1] allow us to determine the physical phase of each species on the surface of Titan. In this work, we include 18 species that are detected in the gas- or the solid-phase on Titan: methane (CH₄), ethane (C₂H₆), ethylene (C₂H₄), acetylene (C₂H₂), propane (C₃H₈), propene (C₃H₆), allene (C₃H₄-a), propyne (C₃H₄-p), diacetylene (C₄H₂), benzene (C₆H₆), hydrogen cyanide (HCN), cyanoacetylene (HC₃N), carbon dioxide (CO₂), acetonitrile (CH₃CN), propionitrile (C₂H₅CN), acrylonitrile (C₂H₃CN), cyanogen (C₂N₂), and dicyanoacetylene (C₄N₂). From the condensation curves constructed in [1], we know that all the 18 detected Titan-relevant organics will condense in the Titan's atmosphere in the solid phase, with only C₃H₈ from the upper atmosphere and evaporated C₂H₆ from Titan's surface condensing into liquids. Then we ask whether these species will maintain in the solid phase or change phase when reaching the surface of Titan. Titan's surface temperature was measured by the Huygens probe to be 93.65±0.25 K near the equator. The seasonal and latitudinal changes in Titan's surface temperature are relatively small according to far-infrared surface brightness temperature observations [8] and global circulation models [9]. Here we assume the surface temperature varies between 90-95 K. We can then calculate and compare the saturation vapor pressure of each species at Titan's surface pressure ($P_{\text{sat-surf}}[X]$) using Table 3 of [1] and the partial pressure of this species ($P[X]$) using their surface mixing ratios, taken from the results of a photochemical model [10]. If the partial pressure of the species is larger than its saturation vapor pressure ($P[X] > P_{\text{sat-surf}}[X]$), the species will be in either the liquid or ice phase. Whether the species will be in the liquid or ice phase will be determined by whether Titan's surface temperature is larger (liquid phase) or smaller (solid phase) than the triple point of the species. If the partial pressure of the species is smaller than its saturation vapor pressure ($P[X] < P_{\text{sat-surf}}[X]$), the species will be in the gas phase.

The species that become liquids or gases at Titan's surface will dissolve into Titan's lakes or become atmospheric constituents. Only species that remain in the solid phase will interact with the lake liquids on Titan (solid-liquid interactions). For these species, we can use their densities and surface properties to evaluate cloud-lake interactions. For the species that are denser than the lake liquids on Titan, we use the wetting theory and the surface free energies of the clouds/lake liquids to determine the contact angles formed between the clouds and lakes. To evaluate the floatability of cloud particles on the lake liquids, we first determine whether the cloud particle is soluble in the lake liquids. If they are soluble, then the floatability problem reduces to between the refractory haze particle and the lake liquids [6], assuming the cloud particle is seeded by the hazes during nucleation. If the cloud species is insoluble, we can then compare the density values of the cloud particle and the lake liquids. Only when the cloud particles are denser than the lake liquids, do we go on to evaluate the contact angle formed between the cloud and the lake liquids and compare it to the threshold contact angle to determine the floatability of the cloud particles.

Results: Most of the higher-order hydrocarbon and all the nitrile ice clouds remain in their solid phase when they deposit on Titan's atmosphere due to the large triple point of these species. These species include: C_2H_2 , C_3H_4 -p, C_4H_2 , C_6H_6 , HCN, HC_3N , CO_2 , CH_3CN , C_2H_5CN , C_2H_3CN , C_2N_2 , and C_4N_2 . Some lower-order hydrocarbons would change phases when they deposit on Titan's surface. CH_4 , C_2H_4 , C_3H_6 , and C_3H_4 -a would go back to the gas phase on Titan's surface. C_3H_8 would condense as a liquid and remain in its liquid phase on Titan's surface. Ethane may turn into a liquid or a gas, depending on the exact surface temperature. These species that are deposited on the surface of Titan may further interact and form "cryominerals" such as co-crystals. Among these species, so far, the detected co-crystals include acetonitrile-acetylene, benzene-acetonitrile, benzene-acetylene, carbon dioxide-acetylene, and benzene-liquid ethane [11]. Future co-crystal investigations could take combinations of the molecules that can remain as solids on Titan's surface as experimental candidates.

Our floatability calculations imply that most organic condensates are wettable by Titan's lake liquids, thus, likely to sink into the lakes, except for C_2H_2 , HCN, and C_2N_2 . The floatability of these three organic compounds depends on the composition of the lake liquids. For C_2H_2 and C_2N_2 , the lake liquids would need to be at least 80% ethane, and the rest of the lake liquids need to be mostly nitrogen to make the contact angle greater than zero. HCN condensates would require at least 60% of

the lake liquids to be ethane to have a non-zero contact angle with the lake surface. The currently known composition of Titan's lakes has less ethane than the required amount for the organic condensates to form a large contact angle. Thus the organic condensates are not likely to float on the surface of Titan's lakes. In summary, if the lake composition is dominated by ethane and the rest dominated by nitrogen, these organic condensates would have non-zero contact angles with the lake liquids, and thus float on the surface of the lake.

Conclusion: We calculated the fate of the simple organic species on Titan's surface, dry and wet. We identified that most simple organics species would stay in the solid phase on Titan's surface, making them solid surface material candidates for the Dragonfly mission. We also find that most simple organics would sink into the methane-ethane-nitrogen lakes of Titan unless they are really fluffy.

References

- [1] Yu, X. et al. *in revision*; [2] Wye, L. C., et al. (2009) *GRL*, 36, 616; [3] Grima, C. et al. (2017) *EPSL*, 474, 20. [4] Cordier, D., & Carrasco, N. (2019) *Nature Geoscience*, 12(5), 315. [6] Yu, X. et al. (2020) *ApJ*, 905, 88. [7] Li et al. (2022) *PSJ*, 3, 2. [9] Jennings et al. (2019) *ApJL*, 877, 1, L8. [9] Tokano (2019) *Icarus*, 317, 337. [10] Willacy et al. (2016) *ApJ*, 829(2), 79. [11] Cable et al. (2021) *Accounts of Chemical Research*, 54(15), 3050.

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