

A SEARCH FOR CYCLIC MOLECULES ON TITAN WITH ALMA. C. A. Nixon¹, M. A. Cordiner^{1,2}, Z. Kisiel³, P. G. J. Irwin⁴, N. A. Teanby⁵, E. M. Molter⁶, A. E. Thelen⁷, M. Y. Palmer^{1,2}, Y.-J. Kuan^{8,9} and S. B. Charnley¹. ¹NASA Goddard Space Flight Center, 8800 Greenbelt Road, Greenbelt, MD 20771, USA, conor.a.nixon@nasa.gov ²Department of Physics, Catholic University of America, Washington, DC 20064, USA. ³Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa, Poland. ⁴Atmospheric, Oceanic and Planetary Physics, Clarendon Laboratory, University of Oxford, Parks Road, Oxford, OX1 3PU, UK. ⁵School of Earth Sciences, University of Bristol, Wills Memorial Building, Queen's Road, Bristol, BS8 1RJ, UK. ⁶Astronomy Department, University of California Berkeley, Berkeley, CA 94720, USA. ⁷Department of Astronomy New Mexico State University PO Box 30001, MSC 4500 Las Cruces, NM 88001. ⁸National Taiwan Normal University, Taipei 116, Taiwan, Republic of China. ⁹Institute of Astronomy and Astrophysics, Academia Sinica, Taipei 106, Taiwan, Republic of China.

Overview: We have made a sensitive spectroscopic search for the small cyclic molecules pyridine (C₅H₅N) and pyrimidine (C₄H₄N₂) in Titan's atmosphere using the ALMA (Atacama Large Millimeter-Submillimeter) telescope. To date, no N-substituted rings have previously been detected in space: finding such molecules has profound astrobiological importance, as pyrimidine (c-C₄H₄N₂) forms the backbone ring for two of the four nucleobases (thymine and cytosine). Our observations did not detect these molecules, and data analysis is ongoing to determine upper limits, important for constraining photochemical models and thereby our understanding of the formation of prebiotic molecules in Titan's atmosphere.

Background: Titan's atmosphere is rich in organic molecules, created by the action of solar UV photons and charged particles from Saturn's magnetosphere acting on the main atmospheric gases, N₂ (98%) and CH₄ (2%) [1]. These primary ingredients are broken apart and recombined to form a plethora of hydrocarbons (C_nH_m) and nitriles (C_nH_mCN) [2], plus some oxygen-bearing species (CO, CO₂, H₂O) by incorporating O⁺ from Enceladus [3]. The largest known molecule on Titan pre-Cassini was benzene (c-C₆H₆), detected by ISO in the middle infrared [4] at 674 cm⁻¹. After the arrival of Cassini in 2004, the Composite Infrared Spectrometer (CIRS, [5]) mapped the spatial distributions of many trace gases [6,7,8] in the neutral atmosphere including benzene, but detected only one new molecule: propene (C₃H₆) [9].

In contrast, the Cassini Ion and Neutral Mass Spectrometer (INMS), by direct sampling of the ionosphere, showed the presence of many new molecules reaching masses of 100 Daltons and beyond [10]. Tentative detections were made of C₆H₂, C₇H₈, C₂H₃CN, C₂H₅CN, C₅H₅N and NH₃, via a signal at the mass of their protonated ions (e.g. NH₃H⁺ at mass 18). However, Cassini's simple mass spectrometer can at best infer molecular formula, but cannot distinguish between isomers. Spectroscopy can resolve this ambiguity: hence it was the CIRS infrared detection of propene in the lower atmosphere that informed whether INMS had

likely measured protonated propene (CH₃CHCH₂H⁺) or cyclopropane (c-C₃H₆H⁺) at mass 43 in the ionosphere. More recently, the first new spectroscopic identification with ALMA of a molecule on Titan has been made by members of our team [11], confirming the presence of C₂H₅CN. Another intriguing case in the INMS data is C₅H₅NH⁺, which could be a protonated form of pyridine, a molecule with large astrobiological significance, or an aliphatic isomer e.g. CH₃CH₂C₂CN. Pyridine is plausible since we already know that another cyclic molecule, benzene, is present.

Observations and Data Analysis: Titan was observed twice on March 2nd and again on March 4th, 2016, for a total time of ~3 hours in four spectral windows in ALMA Band 6, with a spectral resolution of 488 kHz. Modeling was conducted using the NEMESIS radiative transfer computer model [12] with molecular spectroscopic parameters for the cyclic molecules derived from published laboratory and theoretical work [13-15]. Initial analysis shows evidence of known nitriles such as acetonitrile and propionitrile, but emissions of the N-heterocycles were not observed. Efforts are ongoing to improve signal-to-noise ratio by combining datasets and to determine upper limits for these astrobiologically important species.

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