

Submillimeter Detection of CH₃D on Titan

Alexander E. Thelen (1,2), Conor A. Nixon (1), Martin A. Cordiner (1,2), Steven B. Charnley (1), Patrick G. J. Irwin (3), and Zbigniew Kisiel (4).

(1) NASA Goddard Space Flight Center, Maryland, USA, (2) The Catholic University of America, DC, USA, (3) University of Oxford, Oxford, UK, (4) Polish Academy of Sciences, Warszawa, Poland. (alexander.e.thelen@nasa.gov)

Abstract

We detected CH₃D for the first time in the submillimeter using ALMA observations of Titan from 2015. We measured the disk-averaged abundance of CH₃D to be $= 6.157 \times 10^{-6}$ above ~ 130 km, where our measurements are most sensitive. When taken with the CH₄ profile found by the Huygens/GCMS [1], our CH₃D abundance yields a D/H = $(1.033 \pm 0.081) \times 10^{-4}$. The submillimeter detection of CH₃D motivates further ALMA observations to study possible latitudinal variations in Titan's atmospheric CH₄.

1. Introduction

Titan's complex, organic-rich atmosphere is composed primarily of molecular nitrogen (N₂) and methane (CH₄). The photo- and ionic chemistry of these major constituents within Titan's upper atmosphere produces a wealth of hydrocarbon (C_XH_Y) and nitrile (C_XH_Y[CN]_Z) trace species. Although Titan's atmospheric CH₄ reservoir plays a particularly important role in the moon's photochemistry, meteorology, and methane cycle, little evidence of additional sources have been found to balance the rapid photochemical destruction of CH₄ that drives the production of Titan's many trace atmospheric species. CH₄ was directly measured with the Huygens Gas Chromatograph Mass Spectrometer (GCMS) during the probe's descent at $\sim 10^\circ$ S, resulting in a stratospheric ($\sim 75 - 140$ km) volume mixing ratio of 1.48% [1]. Monodeuterated methane (CH₃D) has been measured through a variety of ground- and space-based instruments in the IR (see [2], and references therein), resulting in an average D/H $\sim 1.36 \times 10^{-4}$ for Titan during the Cassini era. Here we present the first detection of CH₃D in the submillimeter, as detailed further in [3]. Using CH₃D as a proxy enables further studies of CH₄ after the end of the Cassini-Huygens mission.

2. Observations

The recent availability of the Atacama Large Millimeter/submillimeter Array (ALMA) Band 8 receivers ($\sim 385 - 500$ GHz) provided a means to detect the $J_K = 2_1 - 1_1$ and $2_0 - 1_0$ transitions of CH₃D at 465.235 and 465.250 GHz (~ 0.644 mm). A short (integration time = 157 s) flux calibration observation of Titan on 02 May, 2015 allowed us to detect both $J = 2 - 1$ transitions of CH₃D at 4.6σ and 5.7σ . The disk-averaged spectrum of Titan and an integrated flux map of both CH₃D $J = 2 - 1$ transitions are shown in Fig. 1. The beam full width at half maximum (FWHM) = $0.767'' \times 0.491''$ for this observation, which is comparable to Titan's angular size on the sky ($\sim 0.7 - 1.0''$, depending on distance and the extent of Titan's substantial atmosphere). Due to the relatively low signal of the CH₃D lines in this observation and the large beam size compared to Titan's disk, these data were unsuitable for nuanced interpretation of latitudinal variations in Titan's atmosphere.

3. Modeling and Results

We used the NEMESIS radiative transfer code [4] to model the disk-averaged spectrum as in previous studies using ALMA flux calibration observations of Titan (e.g. [5, 6]). Line and partition function parameters were obtained from the HITRAN 2012 database and CDMS. Our model contained disk-averaged temperature and gas abundance profiles derived from contemporaneous ALMA observations of Titan [5, 6]. Our initial CH₃D profiles were found by multiplying in situ CH₄ data obtained with the Huygens probe [1] by various D/H ratios found for Titan. These include measurements made during the Cassini era from previous ground-based studies, the Huygens/GCMS, and with Cassini/CIRS, and cover a range of D/H values from $(1.13 - 1.59) \times 10^{-4}$ [2]. Models using all *a priori* abundance profiles converge on a single best-fit spectrum, with scaling factors producing a common CH₃D

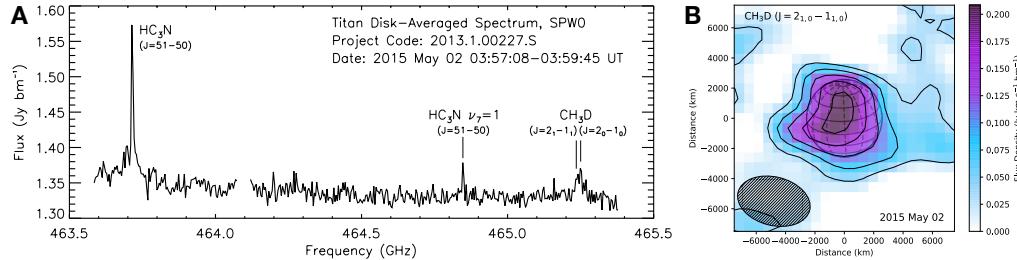


Figure 1: (A) Disk-averaged ALMA flux calibration data of Titan; (B) an integrated flux map of CH_3D emission lines in A. Titan's latitude and longitude lines are shown as gray solid and dashed lines, respectively. Contours are in 1σ intervals. The ALMA beam FWHM is denoted by the hashed ellipse.

profile. Our retrievals were most sensitive between $\sim 100 - 200$ km, where we find the CH_3D abundance to decrease from $(6.455 - 6.157) \times 10^{-6}$. Taken with the Huygens/GCMS measurements of CH_4 , our CH_3D abundance produces a $\text{D/H} = (1.033 \pm 0.081) \times 10^{-4}$.

4. Discussion and Conclusions

The D/H derived by measuring Titan's disk-averaged CH_3D abundance is within the error bars for previous IR measurements throughout the Cassini era and by ground- and space-based facilities, though lower than the average value found through Cassini-Huygens (1.36×10^{-4} [2]) and *Voyager-1* observations. However, further ALMA observations are required for a more rigorous determination of Titan's D/H by measuring the CH_3D abundance profile near the Huygens landing site ($\sim 10^\circ$ S). Additionally, higher spatial resolution observations with ALMA will allow for the study of latitudinal variations in Titan's CH_4 abundance (as in [7]), as the nature of the distribution and replenishment of CH_4 still remain important questions for understanding the chemistry and evolution of Titan's atmosphere after the end of the Cassini mission.

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References

- [1] Niemann, H. B. et al.: Composition of Titan's lower atmosphere and simple surface volatiles as measured by the Cassini-Huygens probe gas chromatograph mass spectrometer experiment, *JGR*, Vol. 115, Issue E12006, 2010.
- [2] Nixon, C. A. et al.: Isotopic ratios in Titan's methane: measurements and modeling, *ApJ*, Vol. 749, pp. 159, 2012.
- [3] Thelen A. E. et al.: Measurement of CH_3D on Titan at submillimeter wavelengths, *AJ*, Vol. 157, pp. 219, 2019.
- [4] Irwin, P. G. J. et al.: The NEMESIS planetary atmosphere radiative transfer and retrieval tool, *JQSRT*, Vol. 109, pp. 1136, 2008.
- [5] Thelen, A. E. et al.: Spatial variations in Titan's atmospheric temperature: ALMA and Cassini comparisons from 2012 to 2015, *Icarus*, Vol. 307, pp. 380, 2018.
- [6] Thelen, A. E. et al.: Abundance measurements of Titan's stratospheric HCN , HC_3N , C_3H_4 , and CH_3CN from ALMA observations, *Icarus*, Vol. 319, pp. 417, 2019.
- [7] Lellouch, E. et al.: The distribution of methane in Titan's stratosphere from Cassini/CIRS observations, *Icarus*, Vol. 231, pp. 323, 2014.