

## Submillimeter Detection of CH<sub>3</sub>D on Titan

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### Abstract

We detected CH<sub>3</sub>D for the first time in the submillimeter using ALMA observations of Titan from 2015. We measured the disk-averaged abundance of CH<sub>3</sub>D to be  $= 6.157 \times 10^{-6}$  above  $\sim 130$  km, where our measurements are most sensitive. When taken with the CH<sub>4</sub> profile found by the Huygens/GCMS [1], our CH<sub>3</sub>D abundance yields a D/H  $= (1.033 \pm 0.081) \times 10^{-4}$ . The submillimeter detection of CH<sub>3</sub>D motivates further ALMA observations to study possible latitudinal variations in Titan's atmospheric CH<sub>4</sub>.

### 1. Introduction

Titan's complex, organic-rich atmosphere is composed primarily of molecular nitrogen (N<sub>2</sub>) and methane (CH<sub>4</sub>). The photo- and ionic chemistry of these major constituents within Titan's upper atmosphere produces a wealth of hydrocarbon (C<sub>X</sub>H<sub>Y</sub>) and nitrile (C<sub>X</sub>H<sub>Y</sub>[CN]<sub>Z</sub>) trace species. Although Titan's atmospheric CH<sub>4</sub> 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 CH<sub>4</sub> that drives the production of Titan's many trace atmospheric species. CH<sub>4</sub> 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 (CH<sub>3</sub>D) 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 CH<sub>3</sub>D in the submillimeter, as detailed further in [3]. Using CH<sub>3</sub>D as a proxy enables further studies of CH<sub>4</sub> 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 CH<sub>3</sub>D at 465.235 and 465.250 GHz ( $\sim 0.644$  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 CH<sub>3</sub>D at  $4.6\sigma$  and  $5.7\sigma$ . The disk-averaged spectrum of Titan and an integrated flux map of both CH<sub>3</sub>D  $J = 2 - 1$  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 CH<sub>3</sub>D 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 CH<sub>3</sub>D profiles were found by multiplying in situ CH<sub>4</sub> 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 CH<sub>3</sub>D

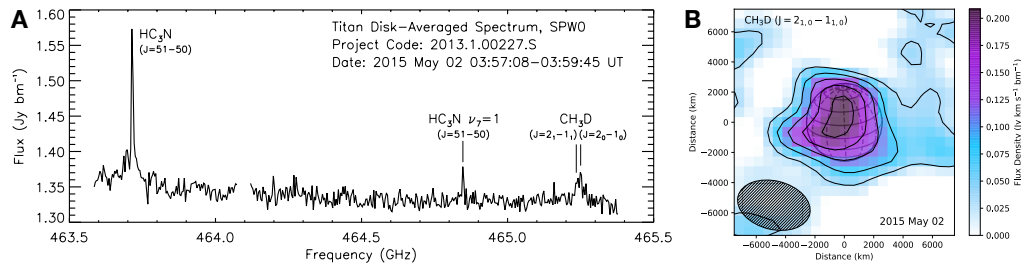


Figure 1: (A) Disk-averaged ALMA flux calibration data of Titan; (B) an integrated flux map of  $\text{CH}_3\text{D}$  emission lines in A. Titan’s latitude and longitude lines are shown as gray solid and dashed lines, respectively. Contours are in  $1\sigma$  intervals. The ALMA beam FWHM is denoted by the hashed ellipse.

profile. Our retrievals were most sensitive between  $\sim 100 - 200$  km, where we find the  $\text{CH}_3\text{D}$  abundance to decrease from  $(6.455 - 6.157) \times 10^{-6}$ . Taken with the Huygens/GCMS measurements of  $\text{CH}_4$ , our  $\text{CH}_3\text{D}$  abundance produces a  $\text{D}/\text{H} = (1.033 \pm 0.081) \times 10^{-4}$ .

## 4. Discussion and Conclusions

The  $\text{D}/\text{H}$  derived by measuring Titan’s disk-averaged  $\text{CH}_3\text{D}$  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 ( $1.36 \times 10^{-4}$  [2]) and *Voyager-1* observations. However, further ALMA observations are required for a more rigorous determination of Titan’s  $\text{D}/\text{H}$  by measuring the  $\text{CH}_3\text{D}$  abundance profile near the Huygens landing site ( $\sim 10^\circ \text{S}$ ). Additionally, higher spatial resolution observations with ALMA will allow for the study of latitudinal variations in Titan’s  $\text{CH}_4$  abundance (as in [7]), as the nature of the distribution and replenishment of  $\text{CH}_4$  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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