Measurement of CH$_3$D on Titan at Submillimeter Wavelengths

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Abstract

We present the first radio/submillimeter detection of monodeuterated methane (CH$_3$D) in Titan’s atmosphere, using archival data from of the Atacama Large Millimeter/submillimeter Array (ALMA). The $J_K = 2_1-1_0$ and $J_K = 2_0-1_0$ transitions at 465.235 and 465.250 GHz ($\sim$0.644 mm) were measured at significance levels of 4.6$\sigma$ and 5.7$\sigma$, respectively. These two lines were modeled using the Non-linear optimal Estimator for MultivariatE spectral analySIS (NEMESIS) radiative transfer code to determine the disk-averaged CH$_3$D volume mixing ratio $= 6.157 \times 10^{-6}$ in Titan’s stratosphere (at altitudes $> 130$ km). By comparison with the CH$_4$ vertical abundance profile measured by Cassini–Huygens mass spectrometry, the resulting value for D/H in CH$_3$D is $(1.033 \pm 0.081) \times 10^{-4}$. This is consistent with previous ground-based and in situ measurements from the Cassini–Huygens mission, though slightly lower than the average of the previous values. Additional CH$_3$D observations at higher spatial resolution will be required to determine a value truly comparable with the Cassini–Huygens CH$_4$ measurements, by measuring CH$_3$D with ALMA close to Titan’s equator. In the post-Cassini era, spatially resolved observations of CH$_3$D with ALMA will enable the latitudinal distribution of methane to be determined, making this an important molecule for further studies.

Key words: planets and satellites: atmospheres – planets and satellites: composition – radiative transfer – submillimeter: planetary systems

1. Introduction

Methane (CH$_4$), one of the primary constituents of Titan’s atmosphere, was first detected by Kuiper (1944) and has since been studied through myriad ground- and space-based observations. The photo- and ionic chemistry of CH$_4$ and Titan’s most abundant atmospheric constituent, N$_2$, in the upper atmosphere are responsible for the large quantity of trace organic species discovered during the Voyager-1 and Cassini eras, and are important for the formation of haze, clouds, and Titan’s methane-based hydrological cycle. However, the source of Titan’s atmospheric CH$_4$ reservoir is still unknown, as are the processes by which it may be replenished.

Titan’s CH$_4$ volume mixing ratio was found to be $5.65 \times 10^{-2}$ near the surface at the location of the Huygens landing site ($\sim$10°S) with the Gas Chromatograph Mass Spectrometer (GCMS), decreasing with altitude to the tropopause ($\sim$45 km); an average stratospheric value of $1.48 \times 10^{-2}$ was measured between $\sim$75–140 km (Niemann et al. 2010). This measurement is compatible with the initial determination of stratospheric CH$_4$ abundance derived from the 7.7 $\mu$m $\nu_4$ band of CH$_4$ by the Cassini Composite Infrared Spectrometer (CIRS), found to be $(1.6 \pm 0.5) \times 10^{-2}$ (Flasar et al. 2005). Subsequent observations of the CH$_4$ $\nu_4$ band were used to probe Titan’s atmospheric temperature with CIRS throughout the Cassini mission by holding the GCMS CH$_4$ profile as latitudinally invariant. However, studies with the Keck II Near Infrared Spectrometer (NIRSPEC) and the Cassini Visual and Infrared Mapping Spectrometer (VIMS) suggested possible variations in Titan’s atmospheric CH$_4$ (Penteado & Griffith 2010; Penteado et al. 2010). Through the combination of two separate CH$_4$ bands in focal planes 1 and 4 of Cassini/CIRS, Lellouch et al. (2014) found the CH$_4$ mole fraction to vary between $\sim$1%–1.5% in the lower stratosphere at 12 locations from 70°N–80°S during Titan’s northern winter ($\sim$2005–2010). This roughly symmetric distribution of CH$_4$ may persist throughout a Titan year ($\sim$29.5 yr), and presents important implications for photochemical and dynamical models of Titan’s atmosphere.

Monodeuterated methane (CH$_3$D) was tentatively identified on Titan by Gillett (1975) in observations of the 8.6 $\mu$m band with the Kitt Peak National Observatory (KPNO), and confirmed by Kim & Caldwell (1982) in combination with data from the Infrared Telescope Facility (IRTF) and the Voyager-1 Infrared Radiometer Interferometer and Spectrometer (IRIS). Later observations with these facilities (Owen et al. 1986; de Bergh et al. 1988; Coustenis et al. 1989; Orton 1992; Penteado et al. 2005), the Infrared Space Observatory (ISO; Coustenis et al. 2003), and through both components of the Cassini–Huygens mission (Bézard et al. 2007; Coustenis et al. 2007; Abbas et al. 2010; Niemann et al. 2010; Nixon et al. 2012) have further constrained Titan’s atmospheric deuterium-to-hydrogen ratio (D/H). With an average value measured to be $1.36 \times 10^{-4}$ during the Cassini era (see Nixon et al. 2012, and references therein), Titan is closer to Earth in terms of atmospheric deuterium enrichment than the giant planets, leading to possible constraints on the formation and sustainability of its atmosphere (Mousis et al. 2002b; Bézard et al. 2014, and references therein).

Due to the dependence on atmospheric temperature for many CH$_4$ observations in the infrared (IR), measurements of Titan’s CH$_3$D abundance may provide a second method for determining possible CH$_4$ variations with latitude, while further constraints on Titan’s D/H will help unravel the history of its formation (Mandt et al. 2009). Previous searches for CH$_3$D in the interstellar medium using submillimeter facilities were
unsuccessful (Pickett et al. 1980; Womack et al. 1996), or provided a tenuous detection of the $J = 1−0$ transition (Sakai et al. 2012). However, the advent of the Atacama Large Millimeter/submillimeter Array (ALMA) and Titan’s relatively large atmospheric CH$_3$D content provide a new method to study this molecule with high spatial and spectral resolution from the ground. Here, we detail the first definitive detection of CH$_3$D at submillimeter/radio wavelengths. Though these measurements were produced from short ALMA flux calibration observations of Titan and do not utilize the full capabilities of the array, they demonstrate the means by which to study Titan’s CH$_4$ distribution and D/H in the post-Cassini era.

2. Observations

Titan is often observed as a flux calibration object for ALMA observations, resulting in many short (~157 s) observations of the moon from 2012 onward. As of 2015, ALMA Band 8 (~385–500 GHz) has been available for use, enabling a search for the $J = 2−1$ and $2_1−1_0$ transitions of CH$_3$D at 465.235 and 465.250 GHz (~0.644 mm). The $J = 1−0$ and $J = 3−2$ transitions at 232.644 GHz (1.289 mm) and 697.690–697.781 GHz (~0.430 mm), respectively, may also be observable with ALMA in Bands 6 and 9. However, the former has a lower line strength than the $J = 2−1$ transitions, and was not detected in the data set analyzed in Thelen et al. (2018) to model the nearby CO $J = 2−1$ transition at 230.538 GHz. As of the time of writing, only two observations of Titan at frequencies covering the CH$_3$D $J = 3−2$ transitions were taken with the lowest frequency resolution usable with ALMA (31250 kHz), and thus the CH$_3$D lines were unresolved (if present). Similarly, observations containing the $J = 2−1$ frequencies use low spectral resolution settings or the Atacama Compact Array, with the exception of an observation on 2015 May 2 at UT 03:57:08, for ALMA Project Code #2017.0.00227.S (where Titan was used for flux calibration). We detected both $J = 2−1$ transitions of CH$_3$D at 4.6σ and 5.7σ in these data from 2015 May, shown in Figure 1. Despite the somewhat coarse spectral resolution inherent to these data (3904 kHz), we resolve both spectral lines of CH$_3$D, which are unresolved in additional archival data at the 15625 kHz resolution. The analogous $J = 2−1$ transitions of the $^{13}$C-substituted form of CH$_3$D at 464.838 and 464.854 GHz (directly abutting the HC$_3$N $ν_2 = 1$ line, Figure 1) were not detected in these data, despite the previous detection of this molecule in the IR (Bézard et al. 2007).

We followed the methodology described in previous works utilizing the ALMA flux calibration data of Titan (e.g., Cordiner et al. 2014; Lai et al. 2017; Thelen et al. 2018, 2019) to obtain disk-averaged spectra and calibrated image cubes. Using the Common Astronomy Software Applications (CASA) package version 5.1.2, we re-ran the ALMA data calibration scripts available with raw data from the ALMA Science Archive$^5$ to ensure that spectral lines in Titan’s atmosphere are not flagged (such as HC$_3$N and CO), and to include the updated flux model for Titan (see ALMA Memo #594$^6$). Imaging was completed using the Hogbom clean algorithm with a pixel size of $0.61 × 0.61$ and a flux threshold of 10 mJy—roughly twice the noise level. The beam FWHM = $0.676 × 0.491$ for this observation, which is comparable to Titan’s angular size on the sky ($0.7−10$, depending on distance and the inclusion of Titan’s substantial atmosphere). Integrated flux maps of the CH$_3$D lines and both nearby HC$_3$N transitions are shown in Figure 2. Due to the relatively low signal-to-noise ratio (S/N) of the CH$_3$D and HC$_3$N $ν_2 = 1$ lines in this observation and the large beam size compared to Titan’s disk, these data are unsuitable for nuanced interpretation of latitudinal variations in Titan’s atmosphere. Despite this, the spatial distribution of both HC$_3$N maps are consistent with contemporaneous data sets analyzed by Cordiner et al. (2017) and Thelen et al. (2019), and the discrepancies in flux found between $ν = 0$ and vibrationally excited HC$_3$N lines discussed in Cordiner et al. (2018).

3. Radiative Transfer Modeling

We extracted a disk-averaged spectrum of Titan by defining a mask of pixels containing at least 90% of Titan’s continuum flux, as in Lai et al. (2017). Using the method in previous studies (e.g., Molter et al. 2016; Thelen et al. 2018) to extract flux from within two times the ALMA point-spread function resulted in a dilution of the disk-averaged CH$_3$D lines in these data. The resulting spectrum is shown in Figure 1. We then converted the disk-averaged flux density into radiance units (nW cm$^{-2}$ sr$^{-1}$ cm$^{-1}$) as described in Appendix A of Teanby et al. (2013) using 24 line-of-sight emission angles to model the flux from the full disk of Titan and the atmosphere up to 1200 km above the surface. The array of field-of-view

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$^5$ http://almascience.nrao.edu

$^6$ http://library.nrao.edu/public/memos/alma/main/memo594.pdf

Figure 1. Complete disk-averaged spectrum of Titan from ALMA observations on 2015 May 2. The spectrum also includes two HC$_3$N lines ($ν = 0$ and $ν_2 = 1$) in addition to the two CH$_3$D $J = 2−1$ transitions at 465.235 and 465.250 GHz. Flux at 464.1 GHz has been flagged (removed) during the ALMA data reduction process due to terrestrial O$_3$ absorption.
averaging points increases in density toward the limb of Titan to account for limb brightening, similar to previous disk-averaged models of Titan’s atmosphere in the submillimeter (Teanby et al. 2013; Thelen et al. 2018). Although additional emission angles may be required to accurately model higher spatial resolution data (e.g., Thelen et al. 2019), summing over 24 annuli was sufficient to model the disk-averaged radiances from these data. Radiances were converted using Titan’s distance of 9.038 au. The sub-observer latitude was 24° 55 and the Doppler shift was −7.5 km s⁻¹; these values were obtained from the JPL Horizons ephemerides generator. We then generated initial radiative transfer models using the Non-linear optimal Estimator for MultivariatE spectral analySIS (NEMESIS) software package (Irwin et al. 2008) to determine any offsets in the continuum level.

Titan’s continuum was modeled using collisionally induced absorption from CH₄, H₂, and N₂ pairs (including isotopes), with coefficients from Borysow & Frommhold (1986a, 1986b, 1986c, 1987), Borysow (1991), and Borysow & Tang (1993). As Titan’s continuum in the submillimeter is largely dependent on the tropopause temperature, we constructed a disk-averaged temperature profile using contemporaneous ALMA measurements from Thelen et al. (2018) in the stratosphere and above, and an interpolation of tropospheric temperatures found using data from the Huygens Atmospheric Structure Instrument (Fulchignoni et al. 2005) and those obtained through Cassini radio occultations (Schinder et al. 2012). This resulted in a small (<5% of the initial radiances), constant offset between the data and model, rectified by multiplying the data by a factor of 1.047. This scaling factor is consistent with previous studies using ALMA flux calibration data (see Thelen et al. 2019, and references therein), and is due to minor discrepancies between our Titan model and the one used in the CASA reduction package for ALMA data (discussed further in Thelen et al. 2018).

To obtain an accurate radiative transfer model of the CH₃D lines emitted in Titan’s atmosphere, we ran NEMESIS in the line-by-line mode over a small spectral range, shown in
Figure 3. CH$_3$D spectral line and partition function parameters were obtained from the Cologne Database for Molecular Spectroscopy (Womack et al. 1996; Müller et al. 2001; Bray et al. 2017). Line broadening and temperature dependence coefficients were obtained from the HITRAN 2012 database (Rothman et al. 2013). Our NEMESIS model also consists of nearby species that may influence the CH$_3$D line shape and nearby continuum, and an appropriate temperature-pressure profile for Titan during northern summer. We thus include N$_2$ and CH$_4$ vertical abundance profiles from Niemann et al. (2010) and Teaney et al. (2013); CO with a constant volume mixing ratio of 50 ppm (see Serigano et al. 2016, and references therein); and HCN, using the 2015 disk-averaged abundance profile found in Thelen et al. (2019). Though nearby emission lines of C$_2$H$_2$CN and C$_3$H$_2$CN do not strongly affect the line shape of the CH$_3$D lines and are undetected in the modeled spectral range of these data, these species were included for completeness using abundance profiles from Lai et al. (2017). The vertical temperature and abundance profiles included in our model are shown in Figure 4.

Due to the somewhat coarse spectral resolution settings of this observation and the relatively low S/N of both CH$_3$D lines (compared to the nearby HC$_3$N line, for example), we opted to find a best-fit spectrum using a simple scaling model (i.e., a constant multiplicative factor) of an a priori CH$_3$D profile. All other modeling parameters, primarily the temperature and additional gas abundance profiles, were held constant, and the CH$_3$D profile was set to retain the initial shape of the a priori input (that is, NEMESIS did not retrieve a continuous vertical profile). Our initial CH$_3$D profiles were found by multiplying in situ CH$_4$ data obtained with the Huygens probe (Niemann et al. 2010) by various D/H ratios. These include measurements made during the Cassini era from previous ground-based studies (Penteado et al. 2005; de Bergh et al. 2012), the Huygens GCMS (Niemann et al. 2010), and with Cassini/CIRS (Bézard et al. 2007; Coulston et al. 2007; Abbas et al. 2010; Nixon et al. 2012), and cover a range of D/H ratios from (1.13–1.59) $\times 10^{-4}$. Spectral models using the D/H ratios = 1.17 $\times 10^{-4}$ and 1.59 $\times 10^{-4}$ from Coulston et al. (2007) and Nixon et al. (2012), respectively, are shown in Figure 3 (magenta and blue spectra); the corresponding CH$_3$D abundance profiles are shown in Figure 4 (black lines). Models using all a priori abundance profiles converge on a single best-fit spectrum shown in Figure 3 (gold), with scaling factors producing a common CH$_3$D profile shown in Figure 4 (gold line). Our retrievals were most sensitive between ~100–200 km, where we find the CH$_3$D abundance to decrease from (6.455–6.157) $\times 10^{-6}$.

4. Discussion and Conclusions

Using archival ALMA flux calibration data of Titan from 2015, we have produced the first definitive detection of CH$_3$D in the submillimeter. While integrated flux maps of the ground ($\nu = 0$) and vibrationally excited ($\nu = 1$) HC$_3$N transitions produced from the same image cube (Figures 2(B), (C)) show spatial distributions consistent with previous studies of Titan with ALMA (Cordier et al. 2017, 2018; Thelen et al. 2019), the integrated flux map of CH$_3$D (Figure 2(A)) shows a lack of significant variation between the poles (less than ~30%). Though this is consistent with a constant CH$_3$D profile (and that of its parent molecule, CH$_4$) with latitude, the low spatial resolution and S/N of the CH$_3$D lines prohibit the interpretation of possible latitudinal variations seen in the higher resolution data acquired with Cassini/VIMS and CIRS (Penteado et al. 2010; Lellouch et al. 2014). We thus measured the disk-averaged abundance of CH$_3$D using the NEMESIS radiative transfer code to be a constant value $= 6.157 \times 10^{-6}$ above ~130 km, where our measurements are most sensitive. When taken with the CH$_4$ profile found by the Huygens GCMS (Niemann et al. 2010), our CH$_3$D abundance yields a D/H = $(1.033 \pm 0.081) \times 10^{-4}$.

The D/H ratio found above is within the errors of previous measurements from ISO, IRTF, KPNO, and the Cassini–Huygens mission (Coulston et al. 2003, 2007; Penteado et al. 2005; Niemann et al. 2010; de Bergh et al. 2012), though generally lower than the average of measurements made during the Cassini era (1.36 $\times 10^{-4}$; Nixon et al. 2012) and from Voyager-1 (1.5 $\times 10^{-4}$; Coulston et al. 1989). The addition of our measurement results in a new weighted mean, D/H = $(1.203_{-0.054}^{+0.057}) \times 10^{-4}$, for observations made during the Cassini / Huygens mission, or utilizing GCMS results. The error bars on our measurement are relative, and only reflect the retrieval errors of our best-fit synthetic CH$_3$D spectrum. As we cannot simultaneously detect CH$_4$ with ALMA, any D/H measurements rely on previous data obtained in the IR by ISO, Voyager-1, Cassini, various ground-based facilities, or in situ data from the Huygens probe. As the GCMS abundance profile of CH$_4$ was determined at the probe’s landing site (~10$^8$S), disk-averaged measurements of Titan with ALMA may not yield a completely comparable D/H to previous, self-consistent measurements with the Cassini–Huygens mission. As shown during the Voyager-1 mission and with the ISO (Coulston et al. 1989, 2003), the measurement of Titan’s D/H ratio is often not straightforward without a well-constrained measurement of CH$_4$. These early results were determined using CH$_4$ abundances = 1.8%–1.9%, which would significantly lower our D/H measurement ($\sim 8.1 \times 10^{-5}$) if used instead of the Huygens/ GCMS results. Further, as there is only one data set on the ALMA archive (at the time of writing) with the spectral settings and resolution capable of resolving both J = 2–1 transitions of CH$_3$D, we were unable to stack measurement sets to produce a higher S/N detection.
As such, the D/H value we report should be taken with caution, as there are many potential sources of error that are difficult to quantify in relatively low spatial resolution ALMA data—including variations in temperature and CH4 abundance with latitude. However, despite our relatively low disk-averaged value of D/H compared to Cassini–Huygens measurements, it remains larger than the D/H values derived from CH4 abundances for Jupiter and Saturn (1.6 × 10−5, Fletcher et al. 2009) by almost an order of magnitude and is more in line with terrestrial D/H measurements in Earth’s oceans (D/H for Vienna Standard Mean Ocean Water is ~1.56 × 10−5; see, e.g., Alexander et al. 2012). Thus, our measurement is consistent with previous observations and models that indicate Titan’s CH4 reservoir did not evolve from a Saturnian D/H value (e.g., through photochemistry or serpentinization reactions within Titan’s interior; Cordier et al. 2008; Mousis et al. 2009). Instead, Titan was possibly formed from an aggregate of planetesimals that were initially enriched in deuterium from interstellar CH4. The isotopic exchange between infalling gas phase CH4 and H2 in the solar nebula eventually resulted in an enhanced D/H value, which was then preserved as CH4 condensed or was trapped within water–ice clathrates in the Saturnian subnebula (Mousis et al. 2002a, 2002b). Titan’s D/H value was then modified through photochemistry, diffusion, atmospheric escape, and the outgassing of CH4 from the interior (Cordier et al. 2008; Mandt et al. 2009), finally resulting in near an order of magnitude greater deuterium enrichment compared to Saturn as we find here.

Despite the uncertainties of our D/H measurement, the detection of CH3D in the submillimeter allows for independent observations of the spatial variation in atmospheric CH4 without the large dependence on simultaneous temperature measurements (as are required in many IR observations). As noted above, the lack of ALMA flux calibration observations covering the J = 2–1 and the adjacent transitions of CH3D presents a need for a targeted study of Titan with longer integration times and adequate spectral resolution. With ALMA’s high spatial resolution capabilities, further studies of CH3D may enable mapping of CH4 down to 100’s of kilometers allowing for a follow-up to the study by Lellouch et al. (2014); higher S/N data will also result in CH3D abundance measurements from a larger range of altitudes. Finally, measuring Titan’s CH3D abundance near the equator allows for a more constrained D/H when determined using data from the Huygens probe.

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