

## Observations of Titan’s Stratosphere During Northern Summer: Temperatures, CH<sub>3</sub>CN and CH<sub>3</sub>D Abundances

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### ABSTRACT

Titan’s atmospheric composition and dynamical state have previously been studied over numerous epochs by both ground- and space-based facilities. However, stratospheric measurements remain sparse during Titan’s northern summer and fall. The lack of seasonal symmetry in observations of Titan’s temperature field and chemical abundances raises questions about the nature of the middle atmosphere’s meridional circulation and evolution over Titan’s 29-yr seasonal cycle that can only be answered through long-term monitoring campaigns. Here, we present maps of Titan’s stratospheric temperature, acetonitrile (or methyl cyanide; CH<sub>3</sub>CN), and monodeuterated methane (CH<sub>3</sub>D) abundances following Titan’s northern summer solstice obtained with Band 9 ( $\sim 0.43$  mm) ALMA observations. We find that increasing temperatures towards high-southern latitudes, currently in winter, resemble those observed during Titan’s northern winter by the Cassini mission. Acetonitrile abundances have changed significantly since previous (sub)millimeter observations, and we find that the species is now highly concentrated at high-southern latitudes. The stratospheric CH<sub>3</sub>D content is found to range between 4–8 ppm in these observations, and we infer

the  $\text{CH}_4$  abundance to vary between  $\sim 0.9 - 1.6\%$  through conversion with previously measured D/H values. A global value of  $\text{CH}_4 = 1.15\%$  was retrieved, lending further evidence to the temporal and spatial variability of Titan’s stratospheric methane when compared with previous measurements. Additional observations are required to determine the cause and magnitude of stratospheric enhancements in methane during these poorly understood seasons on Titan.

## 1. INTRODUCTION

Titan’s atmosphere contains relatively high amounts of methane ( $\text{CH}_4$ ) that, when dissociated along with molecular nitrogen ( $\text{N}_2$ ), forms an expansive network of trace chemical species (see, for example, the reviews by [Bézard et al., 2014](#), [Hörst, 2017](#), and [Nixon, 2024](#)). The distribution of these nitriles and organics both influences and is influenced by Titan’s global circulation ([Hourdin et al., 1995](#); [Rannou et al., 2004](#); [Newman et al., 2011](#); [Lora et al., 2015](#); [Lebonnois et al., 2014](#); [Lombardo & Lora, 2023](#)), which changes with Titan’s long ( $\sim 7$  yr) seasons during which longer-lived photochemical products accumulate at the shrouded winter pole (e.g., [Teanby et al., 2008a](#); [Teanby et al., 2017](#)). These chemical products also impact Titan’s atmospheric energy budget through the absorption and radiation of infrared and UV photons ([Yelle, 1991](#); [Tomasko et al., 2008](#); [Bézard et al., 2018](#)). Thus the temporal and spatial distribution of Titan’s trace species, and the effects of their radiative exchange with the atmosphere, requires investigation of the middle atmosphere (stratosphere and mesosphere;  $\sim 100 - 500$  km) throughout Titan’s 29.5 yr orbit. Great strides in this formidable task have been enabled by the Cassini/Huygens mission and the multitude of measurements presented in recent years on the detection of trace molecules and isotopic ratios ([Bézard et al., 2007](#); [Vinatier et al., 2007](#); [Nixon et al., 2008](#); [Jennings et al., 2008](#); [Coustenis et al., 2008](#); [Jennings et al., 2009](#); [Jolly et al., 2010](#); [Nixon et al., 2012, 2013](#); [Jolly et al., 2015](#)), and seasonal variability in temperature, winds, and composition ([Coustenis et al., 2007](#); [Vinatier et al., 2007](#); [Teanby et al., 2008b,a](#); [Achterberg et al., 2008](#); [Coustenis et al., 2010](#); [Vinatier et al., 2010](#); [Teanby et al., 2010a](#); [Achterberg et al., 2011](#); [Cottini et al., 2012](#); [Teanby et al., 2012](#); [Vinatier et al., 2015](#); [Coustenis et al., 2016](#); [Teanby et al., 2017](#); [Sylvestre et al., 2018](#); [Coustenis et al., 2018](#); [Teanby et al., 2019](#); [Coustenis et al., 2020](#); [Sharkey et al., 2020](#); [Vinatier et al., 2020](#); [Mathé et al., 2020](#); [Sharkey et al., 2021](#); [Achterberg, 2023](#)). These studies form the foundation for continued monitoring of Titan’s atmospheric state during portions of Titan’s year beyond the Cassini mission (2004–2017;  $L_S \sim 300 - 90^\circ$ ), provoking questions and an impetus for further investigations of novel chemical pathways, exogenic energy sources and processes, and the origin and resupply of its crucial methane reservoir ([Tobie et al., 2006](#); [Lunine & Atreya, 2008](#); [Lellouch et al., 2014](#); [Glein, 2015](#); [Davies et al., 2016](#); [Nixon et al., 2018](#); [Miller et al., 2019](#)).

Following the end of the Cassini mission near Titan’s northern summer solstice, ground-based investigations may provide insights into changes occurring in the strato-

sphere and lower mesosphere as influenced by the heretofore unmonitored seasonal changes. Chemical species with both relatively short ( $<1$  yr) and long (e.g., 10s to 100s of yr) photochemical lifetimes can be used as a probe of global scale atmospheric dynamics driven by Titan’s pole-to-pole circulation cell (and near the equinoxes, two equator-to-pole cells). Species such as hydrogen cyanide (HCN) and  $\text{CH}_3\text{CN}$ , with stratospheric lifetimes of 10s of years (Yung et al., 1984; Wilson & Atreya, 2004; Krasnopolsky, 2009, 2014; Dobrijevic et al., 2014; Loison et al., 2015; Willacy et al., 2016; Vuitton et al., 2019), show distributions with lingering enhancements over Titan’s winter pole until the spring. This is largely due to the accumulation of trace species from the subsiding branch of the global circulation cell during winter, which are then confined within the boundary of the circumpolar vortex at latitudes  $>60^\circ$  and persist due to relatively slow or inefficient photochemical destruction (Coustenis et al., 2010; Teanby et al., 2008b, 2009a,b, 2010b; Vinatier et al., 2015; Vinatier et al., 2020; Mathé et al., 2020; Sharkey et al., 2020, 2021; Achterberg, 2023). These distributions can be contrasted with gases of short photochemical lifetimes (e.g., cyano acetylene;  $\text{HC}_3\text{N}$ ), which exhibit rapid enhancements over the fall pole shortly after equinox and are depleted at other latitudes (Thelen et al., 2019b; Teanby et al., 2019; Vinatier et al., 2015; Cordiner et al., 2019; Vinatier et al., 2020).

Additionally, there exists the curious case of Titan’s stratospheric methane, which is thought to be uniformly mixed over seasonal timescales (Wilson & Atreya, 2004; Niemann et al., 2005), but has been shown to potentially be modified by convective injection from localized regions in the troposphere (Lellouch et al., 2014). Though Titan’s methane distribution was thought to be relatively constant above the troposphere and may not show substantial variability with latitude, altitude, and time (often defined using the Huygens measurements presented in Niemann et al. 2010), Lellouch et al. (2014) inferred that the  $\text{CH}_4$  mixing ratio varied from  $\sim 1$ – $1.5\%$  between Titan’s tropical ( $\sim 0$ – $20^\circ$ ) and temperate ( $\sim 30$ – $40^\circ$ ) latitudes through measurements with the Cassini Composite Infrared Spectrometer (CIRS) instrument. Subsequent analysis of 4 Cassini occultations with the Visual Infrared Mapping Spectrometer (VIMS), initially by Maltagliati et al. (2015) and reanalyzed in Rannou et al. (2021) and Rannou et al. (2022), resulted in stratospheric methane measurements closer to  $\sim 1.1\%$ , with localized vertical and latitudinal enhancements. A re-analysis of spectra recorded by the Descent Imager and Spectral Radiometer (DISR) instrument during the descent of the Huygens probe also suggests that the  $\text{CH}_4$  mixing ratio decreases with altitude in Titan’s stratosphere, reaching a value of  $\sim 1\%$  at altitudes above 110 km (Rey et al., 2018). Together, the measurement of  $\text{CH}_4$  and various trace gases allow for the inference of global, and potentially local, circulation and meteorological events that affect the composition and dynamics of the stratosphere, which in turn affect the energy budget of the upper atmosphere and precipitation from the troposphere onto the surface (Yelle, 1991; Hourdin et al., 1995; Rannou et al., 2004, 2006; Cressin

et al., 2008; Tomasko et al., 2008; Mitchell et al., 2009; Mitchell, 2012; Lebonnois et al., 2012; Lebonnois et al., 2014; Lora et al., 2015; Lombardo & Lora, 2023).

In recent years, far-IR and (sub)millimeter observations from facilities such as the Institut de Radioastronomie Millimétrique (IRAM) 30-m telescope and interferometer, Submillimeter Array (SMA), the Atacama Large Millimeter/submillimeter Array (ALMA), and the Herschel Space Telescope have provided the means by which to complement and continue the investigation of Titan’s substantial, complex atmosphere. Early ground- and space-based (sub)mm observations of Titan allowed for the confirmation of H<sub>2</sub>O and HC<sub>3</sub>N following their detections with the Infrared Space Observatory (ISO; Coustenis et al., 1998) and *Voyager 1* spacecraft (Kunde et al., 1981), the first detections of HNC and acetonitrile (or methyl cyanide; CH<sub>3</sub>CN), and the derivation of vertical abundance and temperature profiles (Bézard et al., 1992, 1993; Marten et al., 2002; Gurwell, 2004; Courtin et al., 2011; Rengel et al., 2011; Moreno et al., 2011, 2012a; Rengel et al., 2014; Bauduin et al., 2018; Rengel et al., 2022). Highly resolved spectroscopic measurements provided the means by which to derive Titan’s wind speeds between the upper stratosphere and the thermosphere through Doppler shifts (Moreno et al., 2005; Lellouch et al., 2019; Cordiner et al., 2020; Light et al., 2024). Through the measurement of rotational transitions of thermal tracers such as carbon monoxide (CO) and HCN, ALMA has recently allowed for the derivation of Titan’s vertical temperature profiles throughout the stratosphere, mesosphere, and into the lower thermosphere (Serigano et al., 2016; Thelen et al., 2018; Lellouch et al., 2019; Thelen et al., 2022). Additionally, its high spectral resolution and extensive frequency coverage enable resolved emission line profiles of many organic molecules – some of which were unable to be detected by Cassini in the infrared, including C<sub>2</sub>H<sub>5</sub>CN, C<sub>2</sub>H<sub>3</sub>CN, and others (Cordiner et al., 2015; Palmer et al., 2017; Cordiner et al., 2019; Thelen et al., 2019b, 2020; Nixon et al., 2020). Finally, ALMA has provided the means by which to monitor Titan’s atmospheric CH<sub>4</sub> content in the stratosphere by way of monodeuterated methane (CH<sub>3</sub>D; Thelen et al., 2019a), which has previously been measured in the IR through ground- and space-based facilities and used to derive Titan’s deuterium-to-hydrogen ratio (D/H). Early measurements from *Voyager* and ground-based IR observatories are discussed in Penteado et al. (2005), and references therein, while the values derived from Cassini data are detailed in Nixon et al. (2012). The distribution and modification of these molecular abundance profiles can provide global snapshots of the dynamical state of the atmosphere, while the derived temperature profiles and winds measured from Doppler shifts helps to complete the picture of the seasonal evolution of Titan’s atmosphere (Hörst, 2017; Nixon et al., 2018; Teanby et al., 2019).

Here, we present the analysis of ALMA data acquired in 2022 June ( $L_S \approx 146^\circ$ , during the transition of Titan’s northern hemisphere from summer into fall), designed to investigate both the long-term evolution of Titan’s temperature and chemical abundances. In particular, the measurement of rotational CH<sub>3</sub>D transitions allows for a

comparison to recent Cassini studies showing a  $\text{CH}_4$  distribution influenced by complex tropospheric and stratospheric interplay; further, ALMA allows for the vertical and spatial distribution of  $\text{CH}_3\text{CN}$  to be investigated for the first time, providing an additional tracer of seasonal dynamics (Thelen et al., 2019b). The results of  $\text{CH}_3\text{CN}$  mapping can be compared to HCN and other long-lived chemicals that were measured by Cassini (e.g.,  $\text{CO}_2$ ,  $\text{C}_2\text{H}_6$ ) throughout Titan’s year. These measurements, along with Titan’s temperature field, are investigated here during a period with very limited prior observational coverage. The observational details are described in Section 2, followed by the description of the radiative transfer modeling employed to derive temperature and abundance information in Section 3. The resulting atmospheric retrievals and the discussion, comparisons to prior measurements, and implications are presented in Section 4. A summary of our conclusions is provided in Section 5.

## 2. OBSERVATIONS

The primary array of the ALMA facility is comprised of 50 12-m antennas located on the Chajnantor plateau in the Atacama Desert, Chile. Titan was observed by 44–48 antennas on 2022 June 18 and 29 in ALMA Band 9 (602 – 720 GHz;  $\sim 0.4 - 0.5$  mm), simultaneously targeting the rotational transitions of CO ( $J = 6-5$ ), HCN ( $J = 8-7$ ),  $\text{CH}_3\text{CN}$  ( $J = 38-37$ ), and the  $\text{CH}_3\text{D}$   $J = 3-2$  triplet located between 690 – 710 GHz for ALMA Project #2021.1.01388.S. The observed rotational transitions are detailed in Table 1. The targeted spectral windows were set to resolutions of 488 kHz (HCN), 977 kHz ( $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{D}$ ), and 1129 kHz (CO, continuum window). Millimeter observations at high frequencies are significantly impacted by the Earth’s atmosphere directly above the facility through the reduced atmospheric transmittance and the precipitable water vapor content, which produces interferometric phase artifacts that reduce the image coherence (analogous to optical ‘seeing’ effects). As such, the high frequency transitions of many known trace chemical species have yet to be observed on Titan (or beyond) through interferometry. While Serigano et al. (2016) and Thelen et al. (2019b) observed high frequency transitions of CO ( $J = 6-5$ ), HCN ( $J = 8-7$ ), and  $\text{CH}_3\text{CN}$  ( $J = 37-36$ ), the  $J = 3-2$  rotational  $\text{CH}_3\text{D}$  transitions have yet to be definitively observed in astrophysical environments (though the  $J = 2-1$  transitions were previously detected on Titan – see Thelen et al., 2019a).

Fortunately, the relatively low ( $\sim 0.3-0.5$  mm) precipitable water vapor measurements during the observation dates resulted in low phase scatter, which facilitates observations with the moderately extended ALMA array, which was set to configuration C-5, with maximum antenna separations of up to  $\sim 1.4$  km. While the ALMA data were reduced with the standard pipeline procedures provided by the Joint ALMA Observatory in the Common Astronomy Software Applications (CASA; Jaeger, 2008) ver. 6.2, additional iterative self-calibration and imaging procedures were performed so as to improve the image coherence and signal-to-noise (S/N) ratio, executed similarly to those used for the Galilean Satellites and Giant Planets (de Pater et al., 2019;

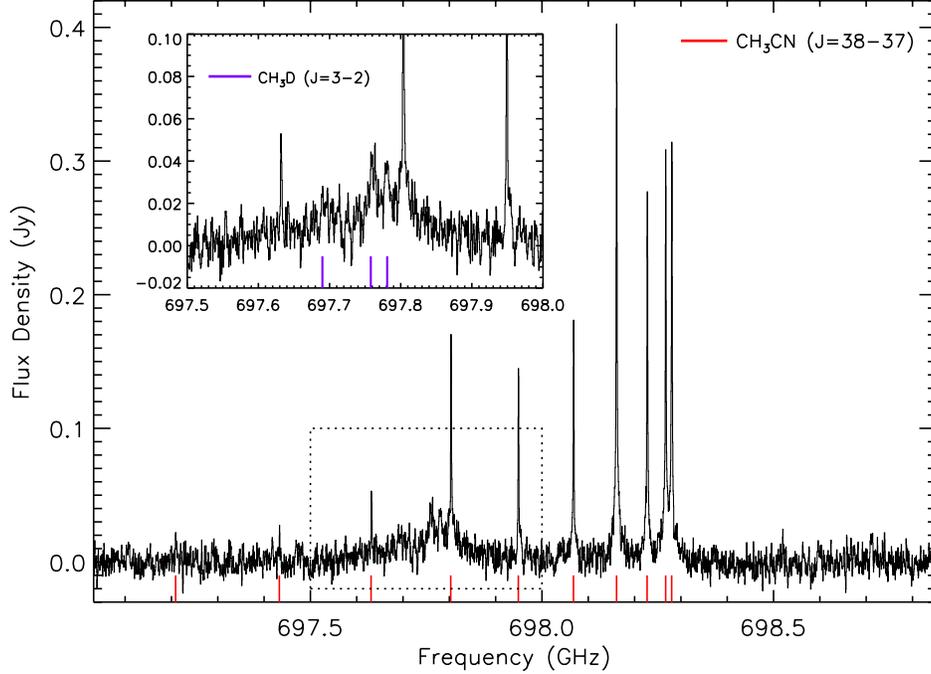
**Table 1.** Observed Spectral Transitions

Species	Transition <sup>a</sup>	Rest Freq. (GHz)	$E_u$ (K)
CO	6 $\rightarrow$ 5	691.473	116.16
CH <sub>3</sub> D	3 <sub>2</sub> $\rightarrow$ 2 <sub>2</sub>	697.691	74.86
	3 <sub>1</sub> $\rightarrow$ 2 <sub>1</sub>	697.759	68.95
	3 <sub>0</sub> $\rightarrow$ 2 <sub>0</sub>	697.781	66.98
CH <sub>3</sub> CN	38 <sub>9</sub> $\rightarrow$ 37 <sub>9</sub>	697.209	1230.80
	38 <sub>8</sub> $\rightarrow$ 37 <sub>8</sub>	697.434	1109.86
	38 <sub>7</sub> $\rightarrow$ 37 <sub>7</sub>	697.632	1003.08
	38 <sub>6</sub> $\rightarrow$ 37 <sub>6</sub>	697.804	910.50
	38 <sub>5</sub> $\rightarrow$ 37 <sub>5</sub>	697.949	832.12
	38 <sub>4</sub> $\rightarrow$ 37 <sub>4</sub>	698.068	767.97
	38 <sub>3</sub> $\rightarrow$ 37 <sub>3</sub>	698.161	718.06
	38 <sub>2</sub> $\rightarrow$ 37 <sub>2</sub>	698.227	682.40
	38 <sub>1</sub> $\rightarrow$ 37 <sub>1</sub>	698.267	661.00
	38 <sub>0</sub> $\rightarrow$ 37 <sub>0</sub>	698.281	653.86

NOTE—Spectral line positions and upper level energies ( $E_u$ ) are taken from the Cologne Database for Molecular Spectroscopy<sup>a</sup> (CDMS; Müller et al., 2001; Müller et al., 2005; Endres et al., 2016). <sup>a</sup>Rotational transitions are denoted as  $Ju \rightarrow Jl$  or  $Ju_{Kl} \rightarrow Jl_{Kl}$ , where  $u$  and  $l$  represent the upper and lower energy states, respectively, and  $K$  represents the angular momentum quantum number.

<sup>a</sup> <https://cdms.astro.uni-koeln.de/classic/entries/>

de Kleer et al., 2021; Camarca et al., 2023; Thelen et al., 2024). First, the CH<sub>3</sub>CN spectral window and a relatively featureless spectral window from the correlator upper sideband at  $\sim 712$  GHz were used to create a single continuum image of Titan by combining data from both ALMA executions. We flagged out all strong spectral line channels from atmospheric trace species and then concatenated the remaining averaged continuum channels using the multi-frequency synthesis settings in the CASA `tclean` algorithm. Using a starting model of a flat or limb-darkened disk at the appropriate brightness temperature of Titan’s Band 9 continuum, we solved for phase solutions as a function of time on this continuum image with successively smaller solution intervals until phase scatter due to noisy antenna baselines were sufficiently minimized; see the reviews in Cornwell & Fomalont (1999), Butler & Bastian (1999),



**Figure 1.** Limb-averaged Titan spectrum, created by averaging 9 separate  $20^\circ$  latitude bins from both eastern and western hemispheres following the combination of both ALMA executions during 2022 June. The spectral resolution was 977 kHz. Spectra were extracted from  $\sim 150$  km above the surface. Data are shown following continuum subtraction. Transitions of the  $\text{CH}_3\text{CN}$  ( $J = 38-37$ ) band from the CDMS catalogue, Doppler-shifted to Titan’s rest velocity, are shown in red for reference; the line marker amplitudes are arbitrary. The dotted box denotes the spectral range of the figure inset, which focuses on the  $\text{CH}_3\text{D}$  ( $J = 3-2$ ) triplet. The  $\text{CH}_3\text{D}$  transitions from the CDMS catalogue are again denoted in vertical purple lines in the inset. As a result of the continuum subtraction, the extent of the pressure-broadened  $\text{CH}_3\text{D}$  band is evident, in comparison to the relatively narrow  $\text{CH}_3\text{CN}$  emission lines.

Brogan et al. (2018), and ALMA Memo #620<sup>1</sup> for further details on self-calibration of bright, compact sources such as planetary disks. Once the continuum phase distribution was on order  $\pm 10\%$ , we applied these phase solutions to the full calibrated spectral line data and performed further image deconvolution on the combined executions to obtain the final spectral image cube. This round of imaging was performed using the CASA `tclean` task with the Högbom algorithm, natural antenna weighting, and  $0.01''$  square pixels, resulting in a final angular resolution (represented by the ALMA beam) of  $0.172 \times 0.148''$  ( $\sim 1000$  km on Titan at the time of observation) with a position angle of  $71.49^\circ$ . Compared to Titan’s angular size of  $\sim 1.0''$  (including its 2575 km solid-body radius and atmosphere up to 1200 km) during the time of observation, this resolution allowed us to observe localized emission from a number of distinct latitude regions ranging from  $\sim 77^\circ\text{S}$  to  $90^\circ\text{N}$ .

<sup>1</sup> Richards et al., ALMA Memo #620: <https://library.nrao.edu/public/memos/alma/main/memo620.pdf>

A latitudinally averaged spectrum extracted from  $\sim 150$  km above Titan’s solid surface, where the  $\text{CH}_3\text{D}$  emission is strong, is presented in Figure 1, showing the stronger  $\text{CH}_3\text{CN}$   $J = 38\text{--}37$  transitions surrounding the broad  $\text{CH}_3\text{D}$   $J = 3\text{--}2$  triplet. Emission maps produced by the integration of channels across this spectral range at every pixel are shown in Figure 2 for the  $\text{CH}_3\text{D}$  and  $\text{CH}_3\text{CN}$  rotational bands, as well as an image of the continuum emission for reference. While the emission from  $\text{CH}_3\text{CN}$  is localized at high-southern latitudes, the  $\text{CH}_3\text{D}$  emission map possesses a significantly lower signal-to-noise ratio, preventing substantial conclusions regarding variations in the  $\text{CH}_3\text{D}$  distribution to be drawn from imaging alone. As in previous studies using ALMA to observe Titan, we extracted spectra at spatially independent regions to determine the variability of vertical profiles with latitude (see Figure 2C). The spatial resolution of these observations enabled the analysis of spectra from approximate  $20^\circ$  latitude bins, which were averaged with the surrounding  $5 \times 5$  pixel grid such as to improve the spectral S/N.

### 3. RADIATIVE TRANSFER MODELING

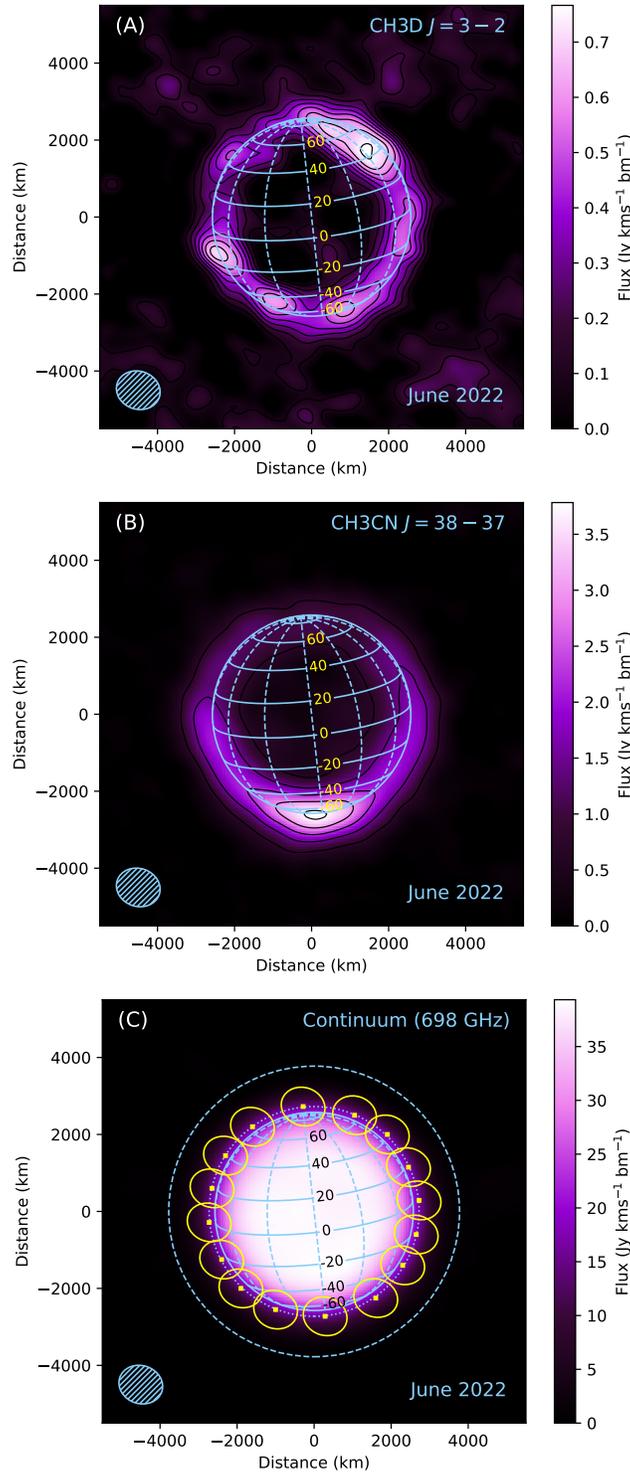
Latitudinally averaged spectra were extracted from the regions denoted in Figure 2C (yellow squares) for use with the radiative transfer package NEMESIS: the Non-linear optimal Estimator for Multivariate spectral analySIS (Irwin et al., 2008; NEMESIS is publicly available online<sup>2</sup>). Wavenumber offsets on order  $1 \times 10^{-5} \text{ cm}^{-1}$  were added to spectra where necessary to account for minor Doppler shifts due to Titan’s wind field (Lellouch et al., 2019; Cordiner et al., 2020); this is  $\sim \frac{1}{3}$  of the ALMA channel spacing. 30 line-of-sight emission angles were calculated for each individual spectrum extraction location so as to correctly model the emission originating from the corresponding ALMA beam-footprint distributed around Titan’s limb (Figure 2C, yellow ellipses); see Thelen et al. (2018) for additional details on the construction of emission angles to represent the ALMA beam shape.

Spectral line frequencies, broadening and temperature dependence parameters, and partition function coefficients were taken from the CDMS and HITRAN database<sup>3</sup> (Rothman et al., 2005, 2013; Gordon et al., 2017, 2022) where available. The  $\text{N}_2$ -broadening parameters for  $\text{CH}_3\text{CN}$  were taken from Dudaryonok et al. (2015), as discussed in Thelen et al. (2019b). Collisionally-induced absorption of  $\text{N}_2$ ,  $\text{CH}_4$ , and  $\text{H}_2$  pairs were parameterized as in previous studies of Titan with ALMA and Cassini/CIRS (Borysow & Frommhold, 1986a,b,c, 1987; Borysow, 1991; Borysow & Tang, 1993). Vertical profiles of these gases were used from Huygens Gas Chromatograph Mass Spectrometer (GCMS) measurements (Niemann et al., 2005, 2010).

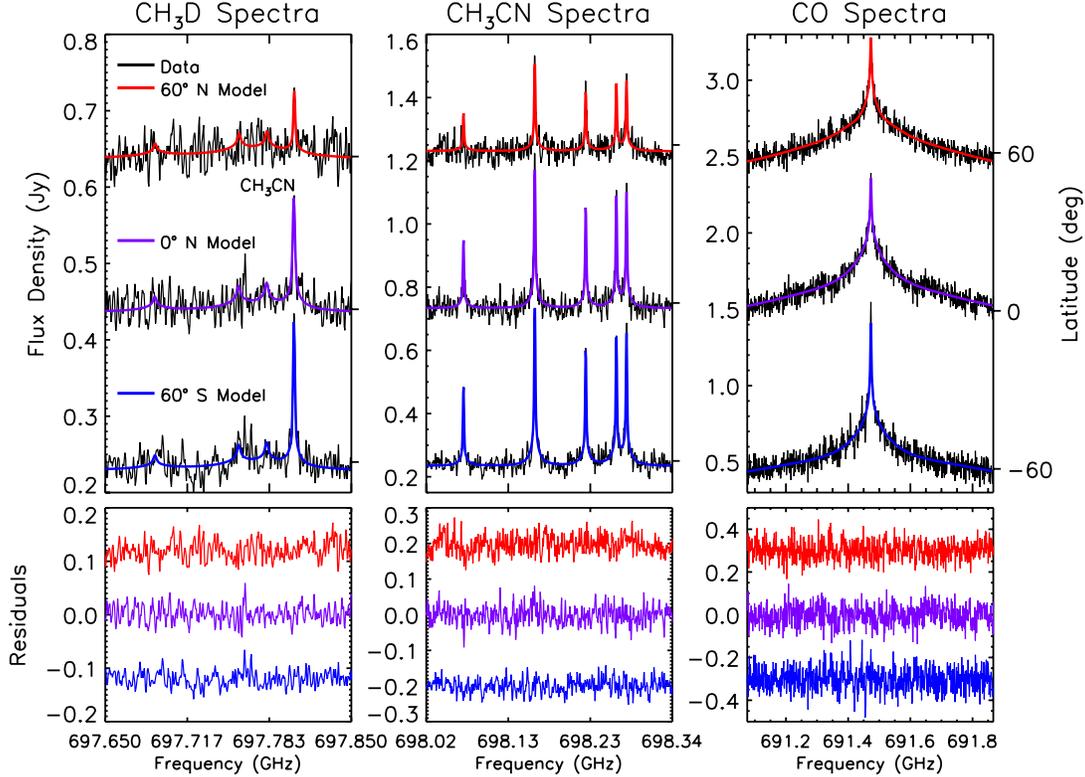
Following spectral extraction and conversion, NEMESIS forward models were generated for spectral regions containing only continuum emission (formed from the above absorption pairs and thermal radiation) to determine constant, multiplicative scal-

<sup>2</sup> <https://nemesiscode.github.io>

<sup>3</sup> <https://hitran.org>



**Figure 2.** Integrated emission (or ‘moment 0’) maps of Titan’s  $\text{CH}_3\text{D}$  (A),  $\text{CH}_3\text{CN}$  (B), and continuum (C) spectra. Panels (A) and (B) correspond to the emission integrated over the spectral transitions shown in Fig. 1. The synthesized ALMA beam size (FWHM of the ALMA PSF) is shown as the hatched ellipse in the lower left; Titan’s solid surface, latitude and longitudes are shown (solid and dashed blue lines). Contours are in increments of  $1\sigma$  (A) and  $10\sigma$  (B). Spectra were extracted for radiative transfer modeling at  $20^\circ$  latitude bins as displayed on the continuum emission map in panel C (yellow squares), and the corresponding area representing the ALMA beam foot-print used to generate synthetic spectra from these individual regions on Titan’s limb are shown (yellow ellipses). Altitudes of 150 km and 1200 km above Titan’s surface are denoted by dotted and dashed blue circles, respectively, on the continuum map.



**Figure 3.** Top row: Representative ALMA data (black) compared to synthetic spectra from the corresponding best-fit NEMESIS models at 60°N (red), the equator (purple), and 60°S (blue) for spectral ranges covering the CH<sub>3</sub>D (left column), CH<sub>3</sub>CN (middle column), and CO (right column) transitions. Spectra are offset by arbitrary, constant factors for clarity (0.2 Jy for CH<sub>3</sub>D; 0.5 Jy for CH<sub>3</sub>CN and CO). The interloping CH<sub>3</sub>CN ( $J = 38_6 - 37_6$ ) transition at 697.804 GHz is denoted in the equatorial CH<sub>3</sub>D spectrum. Bottom row: residual (data–model) spectra corresponding to the data and models in the top row. Residual spectra are offset for clarity (0.12 Jy for CH<sub>3</sub>D; 0.2 for CH<sub>3</sub>CN; 0.3 for CO).

ing factors to apply to the spectra due to flux calibration uncertainties; ALMA flux calibration uncertainties at high frequencies can be as high as 20%<sup>4</sup>. These models were initialized using the stratospheric temperature profile retrieved from recent, unresolved ALMA observations of Titan in 2019 (Thelen et al., 2020), along with tropospheric temperature profiles (which are not expected to show significant seasonal variability) from Cassini Radio Science measurements (Schinder et al., 2020) interpolated to the corresponding latitude regions. The spectral scaling factors were found to be between 0.85–1.15 for each spectral window.

The temperature profiles between the stratosphere and mesosphere were then retrieved using the CO ( $J = 6-5$ ) emission line. Retrievals at each latitude bin were performed by allowing the disk-averaged temperature profile from Thelen et al. (2020) to continuously vary with altitude above  $\sim 100$  km, while keeping the tropospheric temperatures from Schinder et al. (2020) and a nominal CO abundance of  $\sim 50$

<sup>4</sup> See the ALMA Cycle 8-2021 Proposers Guide: <https://almascience.eso.org/documents-and-tools/cycle8/alma-proposers-guide>

parts-per-million (ppm;  $1 \times 10^{-6}$ ), as determined by a number of studies (e.g., de Kok et al., 2007; Teanby et al., 2010b; Gurwell et al., 2011; de Bergh et al., 2012; Rengel et al., 2014; Serigano et al., 2016), held constant. Atmospheric temperatures were varied iteratively with the NEMESIS retrieval algorithm (based on the Levenberg-Marquardt principle – see, e.g., Press et al., 1992) to minimize differences between the data and model spectra (determined by the “cost function”) and subsequently produced parameters that reached a global, reduced- $\chi^2$  minimum (Irwin et al., 2008). The correlation length was taken to be 1.5 scale heights, and though the profiles were allowed to vary up to 1200 km, variations in the temperature profile above  $\sim 600$  km ( $1 \times 10^{-3}$  mbar) did not contribute significantly to minimizing the reduced- $\chi^2$ . The resulting temperature profiles were then used to retrieve the vertical  $\text{CH}_3\text{CN}$  abundance profile at each latitude starting with a combination of abundance profiles from observations by Marten et al. (2002) and photochemical predictions by Loison et al. (2015) above  $\sim 400$  km, as was done with previous ALMA observations (Thelen et al., 2019b). The strongest 5 spectral transitions of the  $\text{CH}_3\text{CN}$  ( $J = 38\text{--}37$ ) band were used to retrieve the vertical profile without interference from the nearby  $\text{CH}_3\text{D}$  ( $J = 3\text{--}2$ ) triplet (see Figure 1).

Finally, the aforementioned temperature and  $\text{CH}_3\text{CN}$  profiles were fixed for  $\text{CH}_3\text{D}$  retrievals. The *a priori*  $\text{CH}_3\text{D}$  profile was generated from the constant stratospheric measurement of  $\text{CH}_4 = 1.48\%$  from the Huygens/GCMS (Niemann et al., 2010) and the D/H from the weighted average of measurements from ALMA and Cassini/CIRS of  $1.2 \times 10^{-4}$  (see Thelen et al., 2019a, Nixon et al., 2012, and references therein). As the individual  $\text{CH}_3\text{D}$  spectra were relatively low signal-to-noise, we performed retrievals on spectra from the East and West hemispheres simultaneously to better constrain the  $\text{CH}_3\text{D}$  abundance. These models were parameterized as a simple scaling of the input profile, as opposed to the continuous retrievals with altitude that were employed for higher S/N spectral lines. Nearby  $\text{CH}_3\text{CN}$  lines were included in the model, and were fit well by the input profiles from the previous retrievals. Representative ALMA data for CO,  $\text{CH}_3\text{CN}$ , and  $\text{CH}_3\text{D}$  are shown in Figure 3 compared to the best-fit NEMESIS models. Residual spectra show that the spectral lines are fit well using the methods described above.

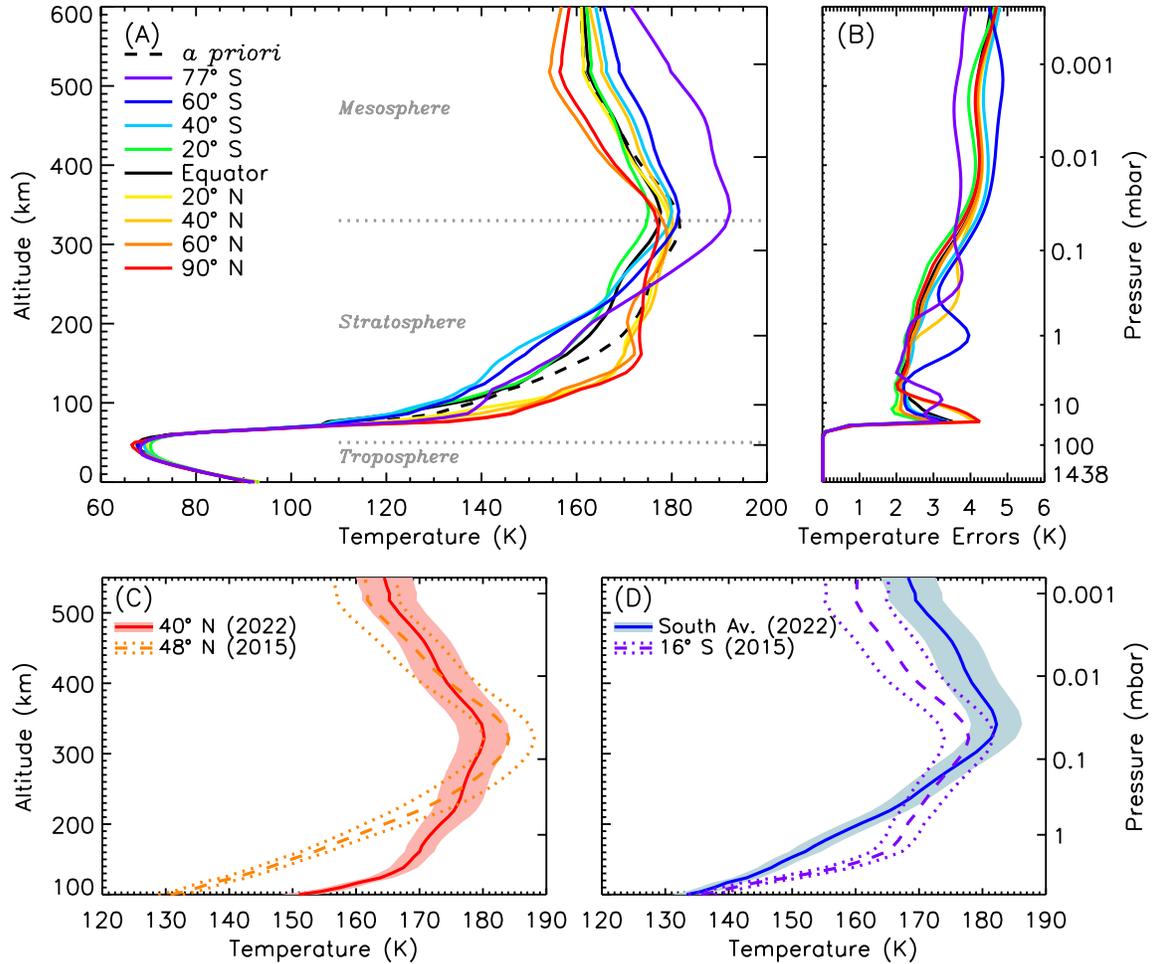
## 4. RESULTS & DISCUSSION

### 4.1. Temperature Profiles

The resulting temperature profiles and corresponding errors retrieved from NEMESIS models of the CO ( $J = 6\text{--}5$ ) transition are shown in Figure 4A and 4B, respectively, throughout the stratosphere and mesosphere ( $\sim 100\text{--}500$  km;  $\sim 10\text{--}1 \times 10^{-3}$  mbar) where the spectral radiance is sensitive to changes in atmospheric temperature. The retrieved temperature profiles show a distinct difference in regions north and south of the equator, particularly at higher latitudes. Below the stratopause (often near  $\sim 300$  km or 0.1 mbar), temperatures from the northern hemisphere (warm

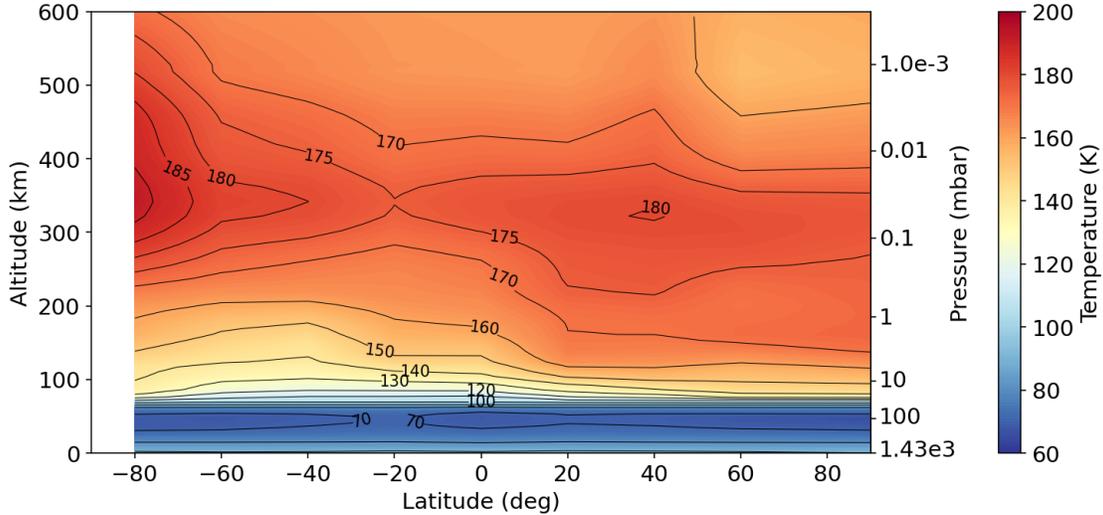
colored profiles in Figure 4A) are elevated compared to those measured at both the equator (black profile) and southern hemisphere (cool colored profiles) by  $\sim 10\text{--}20$  K, particularly between 1 and 10 mbar ( $\sim 100$  to 200 km). Profiles retrieved at  $40^\circ$  and  $60^\circ\text{S}$  are cooler than the equator by  $\sim 7\text{--}10$  K. Titan’s radiative response timescale in the stratosphere is short enough that the atmosphere will respond (i.e. equilibrate) to the increased insolation in the northern hemisphere over  $\sim 1$  Earth yr, well within a Titan season (Flasar et al., 1981). Thus, the dichotomy between temperature profiles in the northern and southern hemispheres follows naturally from Titan’s transition into its northern summer in 2017. While the radiative response time is lower in the mesosphere – so the altitudes above 300 km respond rapidly to insolation – the upper layer of Titan’s pole-to-pole circulation cell also affects these temperatures (see, e.g., Teanby et al., 2008a; Achterberg et al., 2011; Teanby et al., 2012; Vinatier et al., 2015). We find that profiles above 300 km ( $\sim 0.1$  mbar) are largely similar  $\pm 40^\circ$  of the equator, but those at high latitudes show influence of the meridional circulation. Northern hemispheric profiles at high latitudes are cooler than those at lower latitudes above the stratopause, likely due to air rising from below and cooling through adiabatic expansion. The subsiding branch of the circulation cell increases temperatures at the high southern latitudes and, in particular, the highest southern latitudinal profile we can observe here ( $>77^\circ\text{S}$ ) exhibits the highest and warmest stratopause at 190 K between 320–350 km (purple profile in Figure 4A). While the profiles at low southern and northern latitudes are close together in magnitude, the stratopause may be slightly elevated ( $\sim 20$  km) at the highest southern latitudes (blue and purple lines in Figure 4A) compared to the profiles at the highest northern latitudes (orange and red lines). The measurement of temperature profiles in the mesosphere and thermosphere can be achieved using ALMA through the combination of CO and HCN emission lines (Lellouch et al., 2019; Thelen et al., 2022), which we leave to future work for these latitudes.

We derive vertical temperature profiles that are similar to those measured throughout the Cassini mission with the CIRS instrument (Achterberg et al., 2008; Teanby et al., 2010a; Achterberg et al., 2011; Vinatier et al., 2015; Coustenis et al., 2018; Teanby et al., 2019; Coustenis et al., 2020; Vinatier et al., 2020; Mathé et al., 2020), with lower stratospheric ( $<200$  km;  $>1$  mbar) temperatures ranging from  $\sim 130\text{--}170$  K and increasing to a stratopause temperature of  $\sim 180\text{--}200$  K. We observe the continuation of the trend observed through limb and nadir sounding of the atmosphere by CIRS towards the end of the Cassini mission in an elevated, warmer southern stratopause, which mirrors the initial measurements of Titan’s northern polar temperatures during its northern winter at the start of the Cassini mission. This evolution is even apparent through the comparison of the profiles presented here and ALMA observations from 2015 (Figure 4C and 4D), which shows the increase in stratospheric temperatures below  $\sim 200$  km in the north (Figure 4C), the cooling of the stratosphere at these altitudes in the south, and the possibility of a slightly elevated and



**Figure 4.** (A) The resulting latitudinally resolved temperature profiles (solid lines) retrieved using the ALMA CO ( $J = 6-5$ ) spectra. The input disk-averaged profile retrieved from previous ALMA observations (Thelen et al., 2020) is shown (dashed black line). (B) The retrieval errors corresponding to the vertical profiles in panel A. Errors below  $\sim 80$  km are tapered to 0 K to hold the tropospheric temperature values to those derived from the Cassini Radio Science data (Schinder et al., 2020). (C) Comparison of the retrieved temperature profile from Thelen et al. (2018) over a range of northern latitudes (centered at  $\sim 48^\circ\text{N}$ ; dashed orange profile and dotted errors) and the profile presented here at  $40^\circ\text{N}$  (solid red profile and error envelope). (D) Comparison of the retrieved temperature profile from Thelen et al. (2018) representing low southern latitudes ( $\sim 16^\circ\text{S}$ ; dashed purple profile and dotted errors) and an average of the profiles retrieved here from  $20-77^\circ\text{S}$  (solid blue profile and error envelope). The pressure axis on all panels is approximate, represented by the pressures from equatorial latitudes.

warmer southern stratopause (Figure 4D). It should be noted that the vertical and angular resolution of temperature profiles derived through these remote sensing observations is not sufficient to capture potentially stark latitudinal differences towards the poles as observed in other works (e.g. those from the Cassini limb sounding observations – see, for example, Achterberg et al., 2008; Vinatier et al., 2015); as such, the magnitude of the stratopause altitude and temperature variability towards the poles may be somewhat diminished in these ALMA measurements. This is largely



**Figure 5.** Temperatures from Figure 4A, shown as a map as a function of latitude and altitude over the vertical range where our ALMA observations are sensitive. The latitudes below  $80^\circ$  S are not shown due to Titan’s sub-observer latitude at the time of these observations, which shrouds the south pole from view. Temperature contours are shown for reference, as is an approximate pressure grid from equatorial latitudes.

due to the ALMA beam size, which smoothed out the observed atmospheric state over  $\sim 10^\circ$  to  $20^\circ$  latitude ( $\sim 2$  to  $5\times$  that of many CIRS observations), and did not allow for the high degree of altitude sampling as achieved with Cassini/CIRS limb observations (Kunde et al., 1996; Flasar et al., 2004; Nixon et al., 2019).

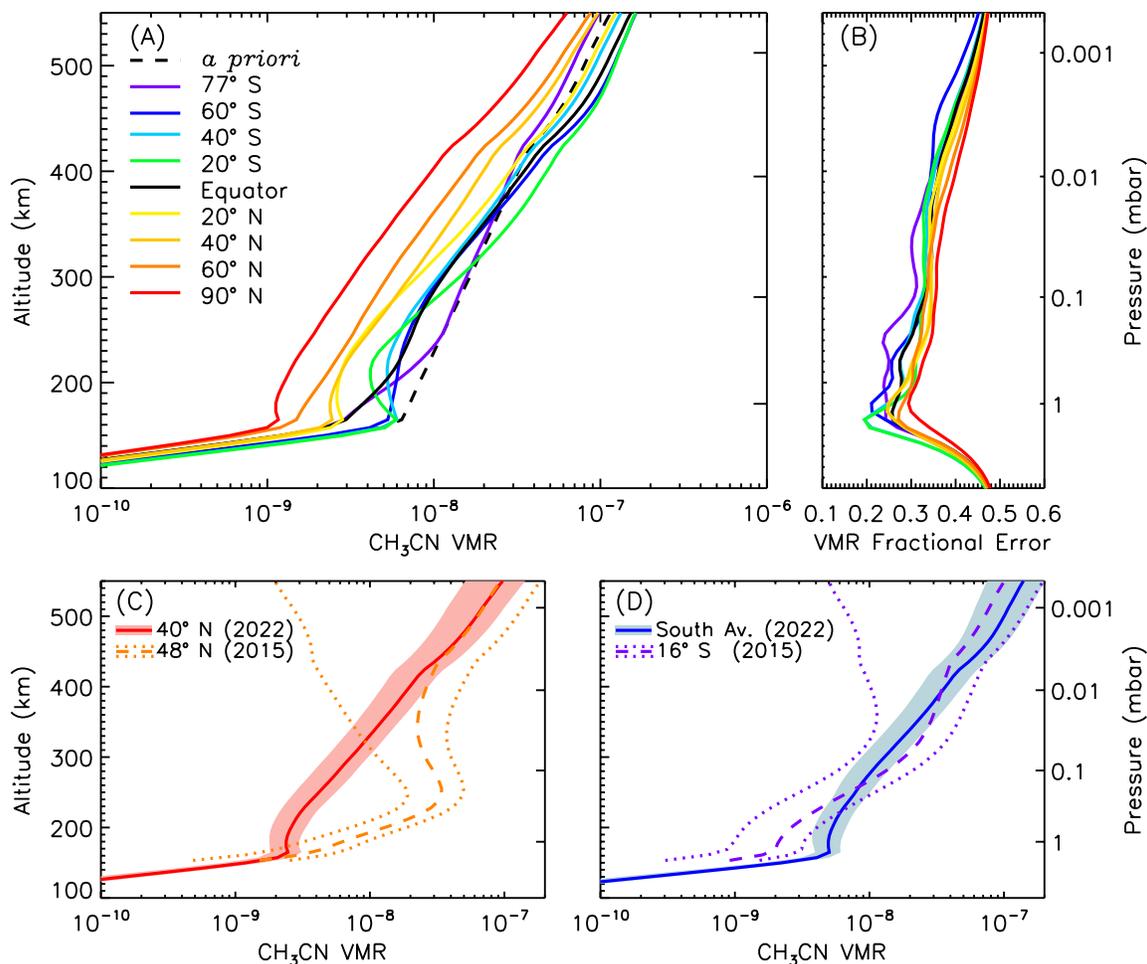
A decrease of northern stratopause temperatures was observed during the course of the Cassini mission as Titan’s northern hemisphere transitioned out of winter and into spring, accompanied by the elevation of southern stratopause temperatures through the adiabatic heating induced by the subsiding branch of the meridional circulation cell – particularly at the south pole – beginning shortly after Titan’s 2009 spring equinox ( $L_S = 0^\circ$ ) (Teanby et al., 2012; Vinatier et al., 2015) and persisting until northern summer solstice ( $L_S = 90^\circ$ ) in 2017 (Teanby et al., 2019; Coustenis et al., 2018, 2020; Vinatier et al., 2020; Mathé et al., 2020; Achterberg, 2023). The circulation of Titan’s middle atmosphere was predicted by modeling efforts and matched well with Cassini observations (see, for example: Crespin et al., 2008; Lora et al., 2015; Shultis et al., 2022; Lombardo & Lora, 2023). For comparison with these circulation model studies, we show our derived temperature profiles as a function of latitude and altitude in Figure 5. Though the viewing geometry of our observations prohibits the retrieval of temperatures at the south pole, the temperature map shown in Figure 5 is in good agreement with the distribution predicted by circulation models of Titan’s northern summer (see Figure 1 in Shultis et al., 2022, or Figure 5 in Lombardo & Lora, 2023) and those found through IR measurements towards the end of the Cassini mission (see e.g., Figure 3 in Teanby et al., 2017; Figure 2 in Vinatier et al., 2020; Figure 6 in Achterberg, 2023); indeed, it is also similar to CIRS measurements derived

during Titan’s northern winter, though now mirrored about the equator (Achterberg et al., 2008, 2011; Vinatier et al., 2015). Previous observations also include a similar stratopause minimum at the low latitudes in the winter hemisphere (see the saddle point at 20°S in Figure 5). Future ALMA observations of Titan at similar angular resolution will allow for the temporal measurement of the atmospheric temperature structure and assess changes over Titan’s northern summer and, in particular, during its autumnal equinox ( $L_S = 180^\circ$ ) in 2025. Here, we may expect the large-scale circulation of the middle atmosphere to break down and eventually reverse, thus completing the seasonal cycle that began with the Cassini observations of Titan in 2004.

#### 4.2. $\text{CH}_3\text{CN}$ Abundances

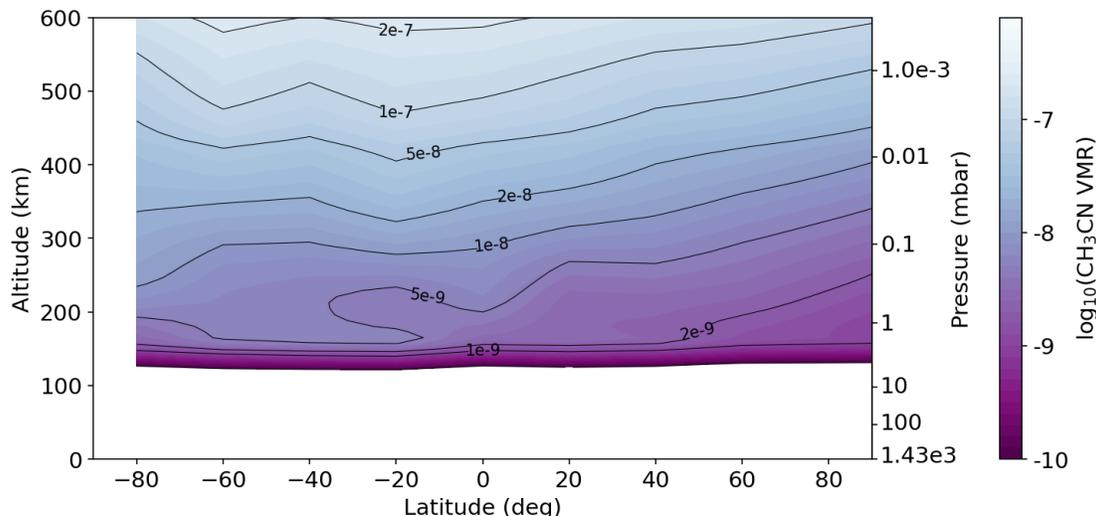
The retrieved  $\text{CH}_3\text{CN}$  profiles are shown in Figure 6A, and their errors (as a fraction of the  $\text{CH}_3\text{CN}$  abundance) in Figure 6B. As discussed in Thelen et al. (2019b), ALMA observations of  $\text{CH}_3\text{CN}$  are not sensitive to variations in abundance below  $\sim 160$  km; this is evidenced by the strong influence of the chosen *a priori* profile (here, taken from Marten et al., 2002) on the retrieved profiles at low altitudes. The retrieved vertical profiles for  $\text{CH}_3\text{CN}$  show a decrease in volume mixing ratio (VMR) with increasing northern latitude, particularly at latitudes north of the equator. The equatorial profile itself is generally in good agreement with the profiles derived by previous (sub)millimeter observations (Marten et al., 2002; Thelen et al., 2019b; Lellouch et al., 2019) and photochemical model predictions above  $>200$  km (Loison et al., 2015; Vuitton et al., 2019). In the stratosphere ( $\sim 250$  km), the  $\text{CH}_3\text{CN}$  abundances at high southern latitudes are enhanced by a factor of  $\sim 5$  compared to the north pole. At higher altitudes ( $>400$  km), where the ALMA data become less sensitive, the abundance profiles are largely similar to the equatorial profile south of 40°N. The differences in the vertical profiles matches the emission map in Figure 2B, though with some additional vertical structure at altitudes  $<200$  km potentially revealing the influence of Titan’s circulation cell on the  $\text{CH}_3\text{CN}$  distribution.

As the photochemical lifetime of  $\text{CH}_3\text{CN}$  in Titan’s middle atmosphere ( $\sim 300$  km) is predicted to be on the order of  $1 \times 10^9$ – $1 \times 10^{11}$  s ( $\sim 32$ – $3200$  Earth yr; Wilson & Atreya, 2004; Loison et al., 2015; Vuitton et al., 2019) – and thus significantly longer than Titan’s  $\sim 29.5$  yr orbital period – the spatial distribution of  $\text{CH}_3\text{CN}$  will be driven dynamically rather than by photodissociation and chemistry. The dynamical or transport lifetime of a species is calculated for individual photochemical species based on vertical and molecular diffusion (Loison et al., 2015; Vuitton et al., 2019), which can then be used to predict the species’ stratospheric polar enrichment when compared to its photochemical lifetime and Titan’s year (Teanby et al., 2009a,b). The observed distribution is further influenced by vertical and horizontal transport from Titan’s winds and circulation. Indeed, the photochemical lifetime of  $\text{CH}_3\text{CN}$  is longer than its dynamical lifetime by a factor of  $\sim 100$  as calculated by the models of Wilson



**Figure 6.** (A) The resulting latitudinally resolved profiles of CH<sub>3</sub>CN abundance (solid lines) retrieved from ALMA CH<sub>3</sub>CN ( $J = 38-37$ ) spectra. The retrievals are shown in a similar altitude range as the retrieved temperature profiles (Figure 4), though the CH<sub>3</sub>CN spectra are not sensitive to abundance variations below  $\sim 160$  km and above  $\sim 450$  km. The *a priori* CH<sub>3</sub>CN profile, constructed from the observations by Marten et al. (2002) and photochemical model predictions by Loison et al. (2015) is shown (dashed black line). (B) The fractional VMR error profiles corresponding to the vertical profiles in panel A. (C) Temporal comparison of the CH<sub>3</sub>CN vertical profile retrieved at 40°N (solid red line and error envelope) to ALMA observations in 2015 (dashed orange profile and dotted errors) from Thelen et al. (2019b). (D) Comparison of an average of southern hemisphere profiles derived here (solid blue line and error envelope) to the vertical profile representing low southern latitudes in 2015 (purple dashed profile and dotted errors) from Thelen et al. (2019b).

& Atreya (2004), Loison et al. (2015), and Vuitton et al. (2019), and comparable to that of HCN. Thus, it is reasonable to expect CH<sub>3</sub>CN to be enriched by a factor of  $<10$  at latitudes  $>60^\circ\text{N}$  by comparison with the enhancements measured by Cassini/CIRS during Titan’s northern winter for HCN and other long-lived molecular species, which were found to be distinctly different than the detected short-lived hydrocarbon species (e.g., C<sub>3</sub>H<sub>4</sub>, C<sub>4</sub>H<sub>2</sub>; Teanby et al., 2008b, 2009b, 2010b). We measure an enhancement factor of  $\sim 1.5$  when comparing the profiles retrieved from spectra at  $\sim 77^\circ\text{S}$  (our



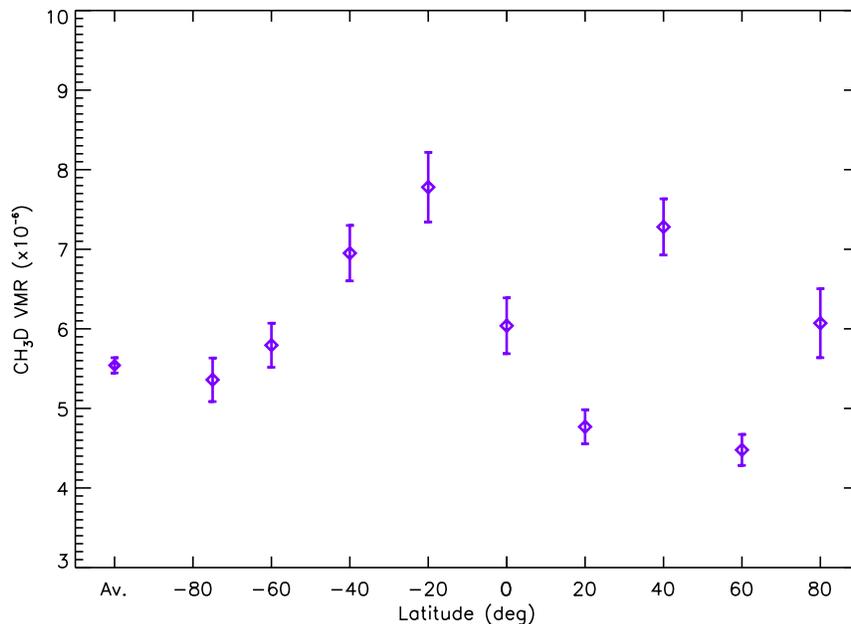
**Figure 7.** Map of  $\text{CH}_3\text{CN}$  abundances as a function of latitude and altitude. The pressure axis is approximate, represented by the pressures from equatorial latitudes.

furthest southern latitude) with that from the equator (see Figure 6A). Despite the range of predicted photochemical lifetimes in Titan’s stratosphere for  $\text{CH}_3\text{CN}$ , our factor is comparable to the predicted enhancement factor of 3 by [Teanby et al. \(2010b\)](#) based on other photochemical species and the photochemical model of [Wilson & Atreya \(2004\)](#). However, without direct measurements of  $\text{CH}_3\text{CN}$  at Titan’s winter pole – obscured by the viewing geometry here – it is difficult to discern the exact enhancement factor. Our current measurement places  $\text{CH}_3\text{CN}$  somewhat in line with the longer-lived (lifetimes  $>100$  yr) hydrocarbon species (e.g.,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ) and  $\text{CO}_2$  as observed during the Cassini mission, which were all observed to be enhanced by factors of  $\sim 1 - 5$  ([Teanby et al., 2008b, 2009a,b, 2010b](#); [Coustenis et al., 2010](#)). This corroborates the predicted dynamical lifetime of  $\text{CH}_3\text{CN}$  by [Loison et al. \(2015\)](#) and the transport lifetime by [Vuitton et al. \(2019\)](#), both of which are  $\sim 91$  yr at 300 km.

As with the temperature profiles, a comparison to previous ALMA retrievals of  $\text{CH}_3\text{CN}$  abundance is shown in Figure 6C and 6D. Here, we see a decrease in northern abundances by a factor of  $\sim 16$  over roughly a Titan season (7 yr). Despite the stark enhancement in emission over the south pole shown in Figure 2B, the abundances at high southern latitudes have only increased by a factor of  $\sim 1.5 - 2$  over this time period. However, it should be noted again that neither of these ALMA observations were able to retrieve the true vertical profile over the south pole, where the accumulation of  $\text{CH}_3\text{CN}$  may be more significant. Additionally, as noted in past works ([Thelen et al., 2019b](#)), the relatively large ALMA beam may preclude us from measuring large enhancements with latitude due to smearing of the emission. Displaying the retrieved abundances as a function of latitude and altitude (Figure 7) shows a shallower  $\text{CH}_3\text{CN}$  abundance gradient than species with shorter lifetimes as observed by Cassini/CIRS (e.g.,  $\text{HC}_3\text{N}$ ,  $\text{C}_2\text{N}_2$ ; [Teanby et al., 2009a,b](#)), but the increased abundances at altitudes  $<200$  km between 20 and 60°S relative to the equator

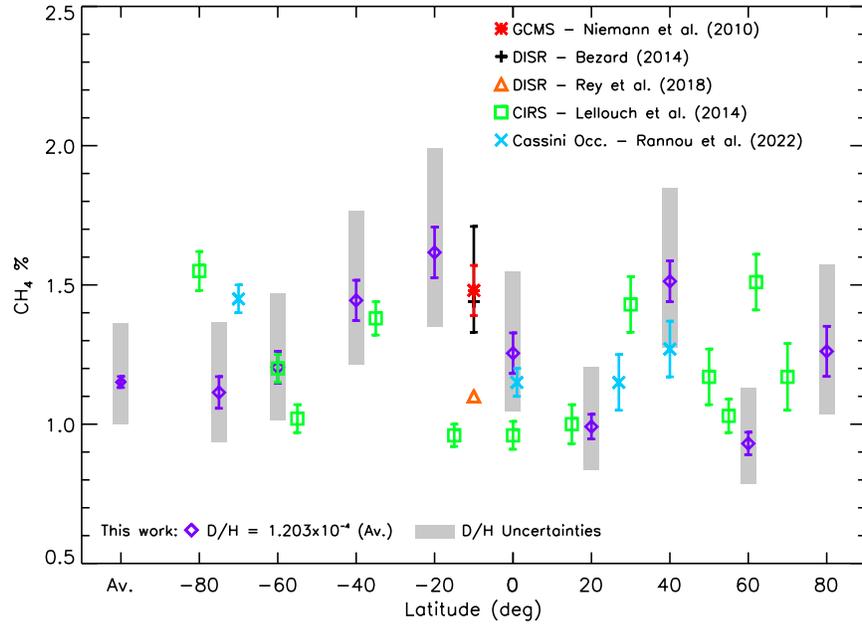
shows similarity to maps of the returning circulation branch in the lower stratosphere, manifesting as a ‘tongue’ of enriched air moving equatorward (Teanby et al., 2008a). This was present in the similarly long-lived HCN during Titan’s northern winter, but surprisingly also in  $C_4H_2$  (Teanby et al., 2008a). Though the predicted photochemical lifetimes of some species may be incorrect, it is also possible that alternative or additional sources of neutral and ion species production, such as galactic cosmic rays, increase the stratospheric abundances (Loison et al., 2015). Additional observations of  $CH_3CN$  in the future may shed light on the changing distribution of this species and the potential for it to track the returning branch of the meridional circulation cell.

#### 4.3. $CH_3D$ Abundances



**Figure 8.**  $CH_3D$  abundance in Titan’s stratosphere (between  $\sim 100$ – $300$  km;  $\sim 0.1$ – $10$  mbar). The retrieval error bars are shown for each data point. Each data point represents the averaged atmospheric  $CH_3D$  VMR for latitudes spanning  $\sim \pm 10^\circ$  (low latitudes) to  $\sim \pm 20^\circ$  (high latitudes) due to the size of the ALMA beam and the sub-observer latitude of Titan ( $\sim 12^\circ$ ), as shown in Figure 2C. The weighted average of all observations is shown (left-most datapoint).

The stratospheric  $CH_3D$  abundances averaged across both hemispheres are shown in Figure 8. As in the emission map in Figure 2A, there is significant spread in the retrieved  $CH_3D$  abundances. The range of measurements,  $\sim 4$ – $8$  ppm, encapsulates the values previously measured by the ISO (Coustenis et al., 2003), ground-based observations (Penteado et al., 2005), and Cassini (Bézard et al., 2007; Coustenis et al., 2007; Abbas et al., 2010; Nixon et al., 2012; Rannou et al., 2022); the weighted average of all latitudes is  $(5.54 \pm 0.10) \times 10^{-6}$  (shown as the left-most point in Figure 8). When taken with the previously derived D/H ratio based on the Cassini/Huygens  $CH_4$



**Figure 9.** Converted  $\text{CH}_4$  abundances as a function of latitude from Figure 8 using the D/H derived in Thelen et al. (2019a) are shown in purple. The weighted average of the converted  $\text{CH}_4$  abundance is shown to the left. The shaded error envelopes illustrate the range of converted  $\text{CH}_4$  abundances after considering the D/H ratios from ALMA ( $=1.033 \times 10^{-4}$ ; Thelen et al., 2019a) and CIRS ( $=1.36 \times 10^{-4}$ ; Nixon et al., 2012 and references therein). The  $\text{CH}_4$  abundances found by the Huygens GCMS (Niemann et al., 2010) and DISR (Bézard, 2014; Rey et al., 2018) are shown (red, black, and orange datapoints, respectively). Green squares show the average measurements of stratospheric  $\text{CH}_4$  derived from Cassini/CIRS by Lellouch et al. (2014). Abundances between  $\sim 150 - 200$  km from Cassini occultation measurements are shown in blue crosses (Rannou et al., 2021, 2022).

measurements, the converted  $\text{CH}_4$  abundances are found to vary between 0.9 – 1.6%, as shown in Figure 9. We find that the values at  $\pm 40^\circ$  and  $20^\circ\text{S}$  exhibit values around the 1.48% level as measured by the Huygens/GCMS (Niemann et al., 2010). The converted weighted average  $\text{CH}_4$  abundance =  $1.15 \pm 0.02\%$  (left-most point in Figure 9), which agrees with previous Cassini averages of  $\sim 1.1\%$   $\text{CH}_4$  in the stratosphere (Lellouch et al., 2014; Rannou et al., 2021, 2022). These, and other disk-averaged observations (e.g., those with the Herschel space telescope – Courtin et al., 2011; Moreno et al., 2012b; Rengel et al., 2014), indicate more variability in Titan’s stratospheric methane than was previously expected; many observations now indicate that the stratospheric methane content is lower than the Huygens/GCMS value derived during the probe’s descent at  $\sim 10^\circ\text{S}$  (Rey et al., 2018).

However, the range of  $\text{CH}_4$  values we derive through  $\text{CH}_3\text{D}$  is complicated by the lack of an independent  $\text{CH}_4$  profile, and thus the D/H uncertainty must be considered as well. The global average  $\text{CH}_4$  value in Figure 9 shows a representative range of the inferred methane abundances when converted using different D/H ratios, which range from  $\sim (1.0 - 1.4) \times 10^{-4}$  as derived and discussed in Nixon et al. (2012) and Thelen et al. (2019a). While the atmospheric D/H ratio is not expected to vary with latitude,

the range of measured D/H values adds additional uncertainty to the CH<sub>4</sub> abundances inferred through the measurement of CH<sub>3</sub>D, increasing our range of converted CH<sub>4</sub> abundances to  $\sim 0.8 - 1.9\%$  with a global weighted average of  $1.15^{+0.21}_{-0.15}\%$ .

The comparison of our converted CH<sub>4</sub> abundances to the variability measured by [Lellouch et al. \(2014\)](#) and [Rannou et al. \(2022\)](#) with Cassini IR and occultation measurements are also shown in Figure 9 (green squares and blue crosses, respectively), as are the abundances derived from the Huygens/GCMS and DISR instruments ([Niemann et al., 2010](#); [Bézard et al., 2014](#); [Rey et al., 2018](#)). While our averaged and equatorial measurements are lower than those measured by [Niemann et al. \(2010\)](#) and [Bézard et al. \(2014\)](#) with the Huygens probe, they are somewhat consistent with the DISR re-analysis by [Rey et al. \(2018\)](#) following the development of newer spectroscopic CH<sub>4</sub> line data. In some instances, our converted CH<sub>4</sub> abundances are in good agreement with those measured with Cassini/CIRS and through VIMS occultations. At 40°S, 20°S, and 40°N, however, the CH<sub>4</sub> values are elevated by  $\sim 0.4\text{--}0.5\%$  (i.e. 30–40% greater than the global average value); these locations also correspond to the enhancements on the integrated emission map (Figure 2A). [Lellouch et al. \(2014\)](#) note that the mixing timescale of CH<sub>4</sub> in Titan’s stratosphere is long enough that enhancements caused by tropospheric injection of methane-enriched air may persist for a large portion of Titan’s year; here, we see that this may explain the agreement of values between these works at certain latitudes, as the data analyzed by [Lellouch et al. \(2014\)](#) originate from Cassini observations almost 15 yr prior to these ALMA observations. However, discrepancies where the ALMA-derived abundances are considerably higher (e.g., 20°S, 40°N) exist. These may be the result of more recent injections that have altered the stratospheric CH<sub>4</sub> reservoir following the Cassini measurements, as cloud activity was observed to be more pronounced at mid-northern latitudes in Cassini/VIMS and Imaging Science Subsystem data following Titan’s spring equinox ([Turtle et al., 2018](#)). Additionally, the equinoctial turnover of Titan’s middle atmospheric circulation cell between these observational epochs may be responsible for redistributing locally enhanced methane to southern latitudes; this may explain the difference between the value retrieved here at 20°S and that found by [Lellouch et al. \(2019\)](#). The dearth of CH<sub>4</sub> measured by ALMA in some locations (e.g., 60°N) compared to Cassini may be the result of the previously observed enhancements relaxing to a well-mixed state due to the changes in circulation during this period.

[Rannou et al. \(2021\)](#) postulated that upwelling from more humid tropical regions of the troposphere breaks through the tropopause and injects higher abundances of CH<sub>4</sub> into specific, localized stratospheric latitudes, which they find at 70°S,  $\sim 165$  km. Comparing the lower stratospheric enhancement evident in the southern CH<sub>4</sub> vertical profile (1.45%, as corrected in [Rannou et al., 2022](#)) to equatorial measurements (1.15%), abundances at higher stratospheric altitudes (1.05% at 250 km), and to the measurements from [Lellouch et al. \(2014\)](#) at a number of latitudes and al-

titudes, they propose a complex stratospheric  $\text{CH}_4$  distribution influenced both by Titan’s meridional circulation and upwelling from localized humid regions of the troposphere based on climate modeling predictions (Rannou et al., 2006) – see Figure 3 in Rannou et al. (2021). As the Cassini CIRS and VIMS observations were acquired during Titan’s northern winter and spring, we may expect both potential new enhancements in the stratosphere from tropospheric injection in the northern latitudes, as well as the redistribution of previously observed enhancements throughout Titan’s long seasonal cycle. Here, our measured enhancements at  $40^\circ\text{N}$  and  $80^\circ\text{N}$  compared to the global average may be the result of upwelling air at humid tropospheric latitudes between  $\sim 30\text{--}60^\circ\text{N}$ , which results in additional  $\text{CH}_4$  distributed to higher northern latitudes and towards the equator. A small, secondary circulation cell moving from mid-northern latitudes poleward has been predicted by circulation models of Titan’s atmosphere during the northern summer (see, e.g., Lombardo & Lora, 2023). We measure  $<1\%$   $\text{CH}_4$  at  $60^\circ\text{N}$ , less than the previous measurement of  $\sim 1.5\%$  in Lellouch et al. (2014), indicating that this may be primarily where the tropospheric upwelling is occurring and bifurcating to poleward and equatorward circulation cells. Indeed, this is where the polar circulation cell of Lombardo & Lora (2023) is observed during northern summer, mirrored from the southern summer circulation cell at  $\sim 50\text{--}60^\circ\text{S}$  in earlier models (Lora et al., 2015). This is invoked by Rannou et al. (2021) to explain their measured stratospheric methane distribution and the relatively methane-dry value measured by Lellouch et al. (2014) at  $\sim 55^\circ\text{S}$ . Meanwhile the dropoff in  $\text{CH}_4$  from the enhancement measured at  $20^\circ\text{S}$  to close to the average at  $80^\circ\text{S}$  may be the result of the reversed meridional circulation distributing  $\text{CH}_4$  towards the southern hemisphere.

Of course, these interpretations should be taken with caution, as the distribution of  $\text{CH}_4$  clearly appears to be complex, evolving, and influenced by both middle and lower atmospheric circulation and climate. Multiple factors contributing to these measurements and interpretations are beyond the capabilities of our ALMA observations, including: independent knowledge of the stratospheric methane itself, or the means to derive the D/H separately from the reliance on previous measurements; the temperature profile of the troposphere, which was taken into account when discussing previous  $\text{CH}_4$  measurements by Cassini and used to infer the tropospheric methane abundance through saturation vapor pressure for comparison to stratospheric values. Currently, the relatively low S/N  $\text{CH}_3\text{D}$  emission also prohibits the retrieval of a vertical profile, which would provide much more insight into the influence of circulation on the interpretation of these measurements (as it does for the other trace atmospheric species). Local vertical enhancements of  $\text{CH}_4$  were found at different stratospheric altitudes compared to the background ( $\sim 1.1\text{--}1.2\%$ ) in the Cassini data analyzed by previous authors (Lellouch et al., 2014; Rannou et al., 2021, 2022), allowing for more complete inferences to be made on the impact of the atmosphere’s dynamical state on the  $\text{CH}_4$  distribution. Our measurements of the  $\text{CH}_4$  abundance should be taken as

averages over a large vertical range ( $\sim 100\text{--}300$  km); as such, the comparison of these values to previous studies at both different times and altitudes complicates an already inconsistent picture. The proposed time-variable influences of circulation, cloud activity, and tropospheric injection remain somewhat speculative until further studies can improve both the D/H certainty and vertical profile of the  $\text{CH}_3\text{D}$  measurements. Still, the aggregate  $\text{CH}_3\text{D}$  measurements imply both a distribution of stratospheric methane that is more complex than thought previously (corroborating the studies by Lellouch et al., 2014 and Rannou et al., 2021), and that the global average  $\text{CH}_4$  abundance in the stratosphere – even when including the known spread of D/H values – is depleted when compared to that of the initial Huygens measurements. This indicates that the single  $\text{CH}_4$  profile from  $\sim 10^\circ\text{S}$  in 2005 ( $L_S \approx 300^\circ$ ) should be used with caution when considering other latitudes and epochs.

## 5. CONCLUSIONS

We have analyzed interferometric observations of Titan in 2022 ( $L_S \approx 146^\circ$ ) following its northern summer solstice, demonstrating seasonal changes in a heretofore sparsely investigated portion of Titan’s year. ALMA Band 9 observations ( $\sim 690\text{--}710$  GHz) enabled the retrieval of abundance and temperature data from multiple latitudinal regions across the disk, which allow us to continue monitoring the atmospheric structure and chemistry after the end of the Cassini mission. Through the analysis of these observations, we find:

- Titan’s stratospheric temperature structure in 2022 is similar to that near the northern summer solstice in 2017, and mirrors the distribution of stratospheric temperatures observed during the northern winter at the start of the Cassini mission (2004;  $L_S \approx 293^\circ$ ).
- For the first time, we retrieve vertical profiles of acetonitrile ( $\text{CH}_3\text{CN}$ ) abundance that exhibit an enhancement in the southern hemisphere. Abundances are enhanced by factors  $\sim 1.5\text{--}5$  compared to the equator and the north pole, but the northern hemisphere abundances have been depleted by up to a factor of 16 since ALMA observations in 2015 (during northern spring).
- Measurements of stratospheric  $\text{CH}_3\text{D}$  sensitive to averaged abundances between  $\sim 100\text{--}300$  km ( $\sim 0.1\text{--}10$  mbar) reveal a complex distribution of monodeuterated methane, which appears at odds with previous measurements in the IR and from the Huygens probe. Using previously derived D/H values, the inferred  $\text{CH}_4$  content of the stratosphere can be found to vary between  $\sim 0.8\text{--}1.9\%$ , with a global average of  $1.15^{+0.21}_{-0.15}\%$ .
- Together, these temperature and abundance measurements are indicative of the influence of Titan’s large, meridional circulation, which warms the upper stratosphere of the winter pole (currently, the south pole) and concentrates the long-lived trace atmospheric species inside the polar vortex. The distribution of

methane is further impacted by Titan’s tropospheric climate, which complicates the interpretation of the CH<sub>4</sub> distribution, but is in general agreement with previous models used to explain the stratospheric distribution during northern winter.

Future observations with ALMA will enable the continued measurement of Titan’s atmospheric structure and composition, including into higher altitudes than were typically possible using Cassini infrared data for some chemical species (Thelen et al., 2022). Higher sensitivity (sub)millimeter investigations of Titan’s CH<sub>3</sub>D may allow for the retrieval of vertical profiles, which will shed additional light onto the impacts of tropo- and stratospheric climate and circulation on Titan’s stratospheric methane.

## 6. ACKNOWLEDGMENTS

Funding for this paper was provided by the NASA ROSES Solar System Observations program for AET, CAN, and MAC. EL, SV, and RM thank the French “Programme National de Planétologie” for funding.

The authors would like to acknowledge M. Palmer for their contribution to the observation proposal. We would also like to acknowledge L. Barcos-Muñoz, R. Loomis, and the North American ALMA Science Center staff for their knowledge and support during the imaging stages of the data reduction.

This paper makes use of the following ALMA data: ADS/JAO.ALMA#2021.1.01388.S. ALMA is a partnership of ESO (representing its member states), NSF (USA) and NINS (Japan), together with NRC (Canada), MOST and ASIAA (Taiwan), and KASI (Republic of Korea), in cooperation with the Republic of Chile. The Joint ALMA Observatory is operated by ESO, AUI/NRAO and NAOJ. The National Radio Astronomy Observatory is a facility of the National Science Foundation operated under cooperative agreement by Associated Universities, Inc.

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