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Spatial and seasonal variations in C_3H_x hydrocarbon abundance in Titan's stratosphere from Cassini CIRS observations

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ABSTRACT

Of the C_3H_x hydrocarbons, propane (C_3H_8) and propyne (methylacetylene, CH_3C_2H) were first detected in Titan's atmosphere during the Voyager 1 flyby in 1980. Propene (propylene, C_3H_6) was first detected in 2013 with data from the Composite InfraRed Spectrometer (CIRS) instrument on Cassini. We present the first measured abundance profiles of propene on Titan from radiative transfer modeling, and compare our measurements to predictions derived from several photochemical models. Near the equator, propene is observed to have a peak abundance of 10 ppbv at a pressure of 0.2 mbar. Several photochemical models predict the amount at this pressure to be in the range 0.3–1 ppbv and also show a local minimum near 0.2 mbar which we do not see in our measurements. We also see that propene follows a different latitudinal trend than the other C_3 molecules. While propane and propyne concentrate near the winter pole, transported via a global convective cell, propene is most abundant above the equator. We retrieve vertical abundances profiles between 125 km and 375 km for these gases for latitude averages between 60°S–20°S, 20°S–20°N, and 20°N–60°N over two time periods, 2004 through 2009 representing Titan's atmosphere before the 2009 equinox, and 2012 through 2015 representing time after the equinox.

Additionally, using newly corrected line data, we determined an updated upper limit for allene (propadiene, CH_2CCH_2, the isomer of propyne). We claim a 3-σ upper limit mixing ratio of 2.5×10^{-9} within 30° of the equator. The measurements we present will further constrain photochemical models by refining reaction rates and the transport of these gases throughout Titan's atmosphere.

1. Introduction

Titan, the largest moon of Saturn, has a CH_4 surface mixing ratio of about 5%, measured by the Huygens GCMS (Niemann et al., 2010), and decreasing with altitude into the stratosphere where it remains constant with altitude at 1–1.5%, as measured in Lellouch et al. (2014). Titan is thought to have many similarities to the Archean Earth, including an atmosphere abundant in N_2 and significant quantities of CH_4 as well as global haze layers which continually shroud Titan and may have occurred intermittently on Earth. While factors like temperature, sources of atmospheric CH_4, and minor atmospheric constituents vary between the two bodies, Titan remains a good analog for studying the atmosphere of the Archean Earth (Arney et al., 2016; Izon et al., 2017).

The global haze on Titan is produced through photolysis of CH_4 as Saturn Magnetospheric Electrons and solar UV photons bombard the upper atmosphere. The products of this process -highly reactive CH_3^-, H^+, and N^+ ions, among others- may then react to form C_2H_6, C_2H_4, and other molecules. As this complex process continues, larger hydrocarbons (C_xH_y) and nitriles ($C_xH_y(CN)_z$) react further to give rise to the 'photochemical zoo' of molecules present in Titan's atmosphere (Yung et al., 1984; Wilson and Atreya, 2004; Lavvas et al., 2008; Loison et al., 2015; Dobrijevic et al., 2016; Willacy et al., 2016).

Titan's 26.7° obliquity (the axial tilt relative to the normal of the orbital plane), comparable to the Earth's 23.5° obliquity, causes variations in the insolation of the moon over the course of a Titan year (about 29.5 Earth years). The resulting seasonal variations in the

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physical state of the atmosphere include molecule abundance (Vinatier et al., 2015; Coustenis et al., 2018), temperature (Achterberg et al., 2011; Teanby et al., 2017), and behavior of the haze layers (Jennings et al., 2012), discussed more in the review by Horst (2017). Noteworthy is the existence of a global circulation cell, which transports warm gases in the summer hemisphere towards the winter pole, where they subside lower into the stratosphere. This downward advection causes adiabatic warming in the winter stratosphere and entrains short-lived gases produced in the upper stratosphere, increasing their abundance lower in the atmosphere. As northern winter evolved to northern spring, this single circulation cell transformed into two circulation cells, upwelling near the equator and downwelling at both poles, as predicted in Hourdin et al. (2004) and observed in Teanby et al. (2012). For additional explanation of Titan's atmospheric dynamics and chemistry, the reader is directed to Brown et al. (2010) and Müller-Woodarg et al. (2014).

Regarding the C_3 hydrocarbons, propane (C_3H_8) and propyne (C_3H_4) were initially detected in Titan's atmosphere after the 1980 Voyager 1 flyby (Hanel et al., 1981) through spectra acquired by the IRIS instrument. Abundances for propyne were first estimated by (Maguire et al., 1981) by comparing the strength of the 633 cm^{-1} Q-branch of propyne to the 721 cm^{-1} Q-branch of acetylene (also ethyne, C_2H_2), and estimated to be on the order of 3×10^{-8}. Propane was modeled in the same paper using a synthetic spectrum constructed for its ν_{21} band, and a disk averaged value of 2×10^{-5} was reported. These values were updated by Coustenis et al. (1989) to $4.4^{+1.7}_{-2.1} \times 10^{-9}$ for propyne and $(7\pm4)\times10^{-7}$ for propane. Further weak bands of propane were detected by the Composite InfraRed Spectrometer (CIRS) aboard Cassini (Nixon et al., 2009). Over three decades later, CIRS spectra were used to make the first detection of C_3H_6 (Nixon et al., 2013), however an exact abundance could not be retrieved from modeling the spectra due to the lack of a spectral line list, although an abundance estimate was made by comparing the intensities of propene and propane lines, discussed more in Section 4.2.

Recent analyses have shown the abundance of propyne to vary strongly with season and latitude. Vinatier et al. (2015), using limb viewing observations, showed the vertical gradient of C_3H_4 increases dramatically over the mid northern latitudes as northern winter moves into northern spring and the polar vortex responds to the changing amount of sunlight. Coustenis et al. (2018), using nadir observations to probe abundance in a narrow altitude range in the middle stratosphere, show a similar trend at latitudes closer to the pole, between 60° and 90° either side of the equator. In the same studies, propane was shown to have a more constant abundance in latitude and time, remaining constant within error bars near 1×10^{-6} throughout the stratosphere, with the exception near the winter pole, where it increases with altitude.

Two C_3 hydrocarbons have yet to be firmly detected on Titan, allene (CH_2CCH_2, isomer of propyne) and cyclopropane ($CH_2CH_2CH_2$, isomer of propene). There was a tentative detection of allene by Roe et al. (2011), however an accurate line list was not available at the time of the study, thus the authors were not able to model the potential allene feature and confirm its detection. In this paper, we discuss members of the C_3H_x series known to be present in Titan's atmosphere-propane (C_3H_8), propene (C_3H_6), and propyne (CH_3C_2H). We also searched for allene and provide a new upper limit for allene in regions close to the equator. This work was enabled by the creation of a propene pseudo-line list for Titan (Sung et al., 2018) and an updated line list for allene (see Section 2.2). We use spectra collected by the CIRS instrument to determine the abundance of propene in Titan's stratosphere. We show latitudinal and seasonal variation in the distribution of propene, propane and propyne. The large number of CIRS observations used allows us to vertically resolve the profile of each gas. We compare the values determined to those predicted by photochemical models of Hébrard et al. (2013), Krasnopolsky (2014), Li et al. (2015), and Loison et al. (2015). Additionally, we use a corrected line list for allene to determine an updated upper limit for the molecule.

2. Methods

2.1. Dataset

CIRS is a Fourier Transform infrared spectrometer, with three focal planes spanning the 10 cm^{-1} - 1500 cm^{-1} spectral region (Jennings et al., 2017). We use spectra acquired by Focal Plane 3 (FP3, 580 cm^{-1}-1100 cm^{-1}) and Focal Plane 4 (FP4, 1050 cm^{-1}-1500cm^{-1}), two parallel arrays of 10 detectors each. Limb observations were performed at a spectral resolution of 0.5 cm^{-1} at distances between 10^5 km and 2×10^5 km from Titan, during which time each focal plane was positioned normal to Titan's surface, such that each detector sampled a different altitude. The arrays were centered at 125 km for between one and two hours and were then moved away from Titan's surface to stare at a central altitude of 350 km for a similar amount of time. The footprint of each detector (the vertical resolution) on Titan's atmosphere varied between 27 km and 54 km depending on the distance to the moon. The size of the footprint was comparable to Titan's atmospheric scale height, and thus allows us to vertically resolve physical characteristics of the atmosphere.

The C_3H_6 ν_{19} band detected in Nixon et al. (2013) at 912.67 cm^{-1} sits between several C_2H_4 emissions, and on top of a broad C_3H_8 band. To increase S/N to the point where we can model this feature, we divide the CIRS dataset into six time-latitude bins, where in each bin the temperature varies less than 15 K. We make the assumption that over the time and latitudes covered in by each bin, Titan's stratosphere has similar temperature and molecular abundance profiles. Spectra in each bin are averaged together to reduce random noise in the data before modeling. Each bin includes data from between three and seven flybys (or between 187 and 728 spectra). We use two time periods - the pre equinox time from 2005 to 2009 (just before the northern vernal equinox of August 2009) and the post equinox time 2012 through 2015. During the time just after the northern vernal equinox, Cassini was in a very low inclination orbit relative to Saturn. Limb observations on Titan were focused on the polar regions, as Cassini was able to view these regions of the atmosphere continuously during a Titan flyby. We therefore do not include data from just after the equinox, as no limb data exists for the latitude regions we model in this work. In each time span, we combine observations representative of three latitude regions - northern, equatorial, and southern.

In our averages, we include data from 20° to 60° for both hemispheres, and within 20° of the equator. The former two bins represent the mid-latitudes, and the third bin represent the equatorial atmosphere. While the latitude boundaries for observations we include are the same before and after equinox, the physical distribution of included observations varies. As an example, in the pre-equinox time, the northern bin contains observations from 24°N through 54°N, whereas post-equinox we have observations only between 25°N and 48°N. The distribution of observations used is shown in Fig. 1 as black dots. The boundaries for each time-latitudinal bin are drawn as black boxes enclosing observations. We exclude observation centered at latitudes closer than 60° to either pole because temperature begins to vary strongly with latitude in these regions. Including these spectra in our averages would make the resultant spectra very difficult to model and obscure details of finer latitudinal variations in the retrieved profiles.

A summary of the data used is in Table 1.

2.2. Spectral line data

Molecular line lists used are described in Table 2.

2.2.1. Updated allene linedata

No allene line lists are currently present in the HITRAN or GEISA databases. Coustenis et al. (1993) initially investigated the detectability