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Search for methane isotope fractionation due to Rayleigh distillation on Titan

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ABSTRACT

We search for meridional variation in the abundance of CH_3D relative to CH_4 on Titan using near-IR spectra obtained with NIRSPAO at Keck, which have a photon-limited signal-to-noise ratio of ∼50. Our observations can rule out a larger than 10% variation in the column of CH_3D below 50 km. The preferential condensation of the heavy isotopologues will fractionate methane by reducing CH_3D in the remaining vapor, and therefore these observations place limits on the amount of condensation that occurs in the troposphere. While previous estimates of CH_3D fractionation on Titan have estimated an upper limit of −6‰, assuming a solid condensate, we consider more recent laboratory data for the equilibrium fractionation over liquid methane, and use a Rayleigh distillation model to calculate fractionation in an ascending parcel of air that is following a moist adiabat. We find that deep, precipitating convection can enhance the fractionation of the remaining methane vapor by −10 to −40‰, depending on the final temperature of the rising parcel. By relating fractionation of our reference parcel model to the pressure level where the moist adiabat achieves the required temperature, we argue that the measured methane fractionation constrains the outflow level for a deep convective event. Observations with a factor of at least 4–6 times larger signal-to-noise are required to detect this amount of fractionation, depending on the altitude range over which the outflow from deep convection occurs.

1. Introduction

Titan's hydrological cycle is an interesting combination of atmospheric and surface processes, and it is important for understanding the climate; for example, see the review by Mitchell and Lora (2016). Unlike on Earth, where the water of the hydrological cycle is primarily in the condensed phase on the surface, Titan's supply of methane is stored mostly in the atmosphere as vapor (Lorenz et al., 2008). The column of methane vapor is equivalent to 5 m of liquid at the surface (Tokano et al., 2006). The large atmospheric reservoir contributes to the fact that the phase transitions of methane are a significant part of the energy transport in the atmosphere (Mitchell et al., 2009). The evaporation, circulation, and condensation of atmospheric methane redistributes the energy that is input as short wavelength solar radiation near to the equator, and moves it such that the outgoing long wavelength radiation at the top of the atmosphere is emitted nearly isotropically (Mitchell, 2012).

Condensation and evaporation are critical for determining which regions of the surface are dry or wet, with net evaporation drying the equatorial regions (Lora et al., 2015; Mitchell, 2008). While axisymmetric models of circulation predict the preponderance of ponding near the poles, they do not explain why the northern polar surface has significantly more and larger lakes than in the south (Hayes et al., 2008; Stofan et al., 2007; Turtle et al., 2009). One explanation for the asymmetric distribution of polar lakes on Titan is Saturn's orbital eccentricity, which is thought to drive the seasonally-averaged preferential evaporation from the south (Aharonson et al., 2009). Tropospheric eddies, which models suggest are more vigorous in the south, are important for this process, as they pump the moisture that is evaporating from the surface up to higher altitudes and towards lower latitudes, and supply vapor to the upper atmosphere where the meridional overturning circulation takes place (Lora and Mitchell, 2015). Measuring the condensation of methane in the atmosphere, and how it changes with time, is one way to evaluate whether this explanation of the distribution of lakes is correct.

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Indications of precipitation (Ádámkovics et al., 2009, 2007; Mitchell et al., 2011; Perron et al., 2006; Tokano et al., 2006; Turtle et al., 2011) and the observations of clouds (Brown et al., 2002; Roe, 2012; Roe et al., 2002) demonstrate that condensation is occuring in the atmosphere, but measurements of methane vapor are challenging. The Cassini–Huygens probe gas chromatograph mass spectrometer (GCMS) is the canonical measurement of methane (Niemann et al., 2010), and is often used as the point of reference for measurements at other locations and at other times. Cassini/CIRS spectra in the thermal IR are sensitive to both the methane abundance and temperature in stratosphere, and the mole fraction measured by the GCMS is used to retrieve thermal profiles (e.g., Flasar et al., 2005; Achterberg et al., 2011). Lellouch et al. (2014) suggest that CIRS spectra can be used to measure the stratospheric methane abundance, since the mid- and far-IR lines of methane have different sensitivities to the thermal profile, and they find mole fractions near ∼85 km altitude of ∼1.0% at low latitudes, contrary to the GCMS. At 70 N, where using the CIRS lines to constrain the temperature is challenging, Lellouch et al. (2014) find a mole fraction of ∼1.0%, whereas Anderson et al. (2014) interpret the same observations with a temperature profile that was independently determined with Cassini Radio Science Subsystem (RSS) and find a mole fraction of ∼1.5%. Near-IR measurements made with the Upward Looking Infrared Spectrometer (ULIS) of the Descent Imager/Spectral Radiometer (DISR) are consistent with the GCMS, and it has been suggested that the discrepancy with CIRS is due to uncertainties in methane line parameters (Bézard, 2014). On the other hand, the near-IR measurements of methane abundance are sensitive to properties of the atmospheric aerosol (Ádámkovics et al., 2016; Penteado et al., 2010). A method of measuring condensation that does not necessarily rely on the mole fraction would be a valuable complement to these techniques.

Condensation and evaporation impart an isotopic signature on a system because the rates of chemical and physical processes are different among isotopologues, due to the differences in mass, bonding, and zero point energies. In a closed system at equilibrium, the vapor pressures of different isotopologues are a measure of the difference in these rates. For a physical system like a parcel of air, where the condensate can be removed from the system, the fractionation can be larger still, as the fractionated condensate leaves the system. Rayleigh fractionation is therefore a signature of the magnitude and temperature at which evaporation and condensation occur, and measurements of ^{18}O and D in water are commonly used in interpreting properties of Earth's hydrological cycles (Dansgaard, 1964). Isotopic fractionation of condensible liquids is of considerable interest not only for characterizing the terrestrial water cycle (e.g., see review by Xi, 2014), but also for constraining the martian water cycle (e.g. Montmessin et al., 2005; Villanueva et al., 2015; Encrenaz et al., 2016). Similarly, the hydrological cycle on Titan can be informed by measurement of the isotopic composition of methane.

Recent measurements of the methane humidity in the lower atmosphere were made using spatially-resolved spectra in the 1.5 μm (H-band) spectral region (Ádámkovics et al., 2016). Here we present further study of these spectra in the Section 2, focusing on a detailed uncertainty analysis. The H-band is sensitive to two isotopologues of methane, offering the possibility of detecting variation in the strength of CH_3D spectral features relative to those of CH_4. While systematic instrumental noise and uncertainties in the gas-phase opacity are important, searching for variation in CH_3D relative to CH_4, and in spectra at one location relative to another, means that we can take into account the systematic effects. In Section 3 we describe the S/N required to measure a given magnitude of fractionation, and in Section 4 we discuss these results interpreted with a Rayleigh fractionation model, where we estimate the magnitude of fractionation in a parcel of air with condensation.

2. Methods

2.1. Observations

The Near-InfraRed SPECctrometer (McLean et al., 1998) with adaptive optics (NIRSPAO) was used at W. M. Keck Observatory on 17 July 2014 UT to observe Titan with a spectral resolving power of $R \approx 25,000$ and a spatial sampling of 0.018"/pixel along the slit. A single North-to-South position along the central meridian was integrated for 45 min. We analyze spectra from one echelle order centered near 1.55 μm. Additional details of these observations, including the data reduction and calibration with supporting datasets, are described in Ádámkovics et al. (2016).

2.2. Radiative transfer model

Synthetic spectra are generated by defining 20 atmospheric layers, with properties that are determined primarily by measurements made with instruments on the *Huygens* probe. The layers have boundaries (levels) that are evenly spaced in pressure, with 10 levels above and 10 levels below 300 mbar (see Table 2 in Ádámkovics et al., 2016). The top of the atmosphere is set at zero optical depth. We use measurements of the temperature, pressure, methane abundance, and aerosol structure to determine the gas and scattering opacity in each layer. The methane below 35 km and aerosol above 65 km are assumed to vary with latitude, as detailed in Ádámkovics et al. (2016). Methane is increasing linearly from 40N toward the south, reaching a 30% enhancement at 40S, while the aerosol is increasing in opacity toward the north. The *Huygens* temperature profile is used at all latitudes. CH_4 and CH_3D line opacities are from the HITRAN 2012 database (Rothman et al., 2013). The discrete-ordinate-method radiative transfer (DISORT; Stamnes et al., 1988) is implemented in Python (PyDISORT) and used to solve the radiative transfer through the model atmosphere and simulate the observed flux.

Each (x, y) pixel on the detector maps to a wavelength and latitude (λ_x, ϕ_y) for the observed flux, $I_{obs}(\lambda_x, \phi_y)$. We use the radiative transfer model to calculate the flux $I_{calc}(\lambda_x, \phi_y)$ corresponding to this wavelength and location, taking into account the viewing geometry and spatial variation in surface albedo and hazes (Ádámkovics et al., 2016). An example spectrum from one NIRSPAO pixel along the slit (out of a total of 44 that cover the disk of Titan), is compared with the radiative transfer model calculation in Fig. 1.

2.3. Uncertainty analysis

By inspecting a 300 s exposure, we find the background count rate at echelle Order 49 to be 0.21 DN/s, while the count rate on Titan ranges from 0.08 to 0.63 DN/s, in the dark and bright spectral regions, respectively. Using a NIRSPAO dark current of $0.7e^-$/s/pix, gain of $5.7e^-$/DN, read noise of $23e^-$, and total 9×300 s exposure time, the counting-limited signal-to-noise ratio S/N per pixel ranges from 19 in the dark regions to 87 where Titan is bright. We'll use the mean value to characterize the entire spectrum as S/N ≈ 50. In units of reflectivity, which cover a range of roughly 0.03 to 0.12 I/F, this level of noise corresponds to ∼0.0015 I/F per pixel and sets the limit for the expected residuals when comparing these observations to our models.

The residual for each pixel is defined with the following notation,

$$r_{\lambda,\phi} = I_{obs}(\lambda_x, \phi_y) - I_{calc}(\lambda_x, \phi_y), \quad (1)$$