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ISOTOPIC RATIOS IN TITAN'S ATMOSPHERE FROM *CASSINI* CIRS LIMB SOUNDING: HC_3N IN THE NORTH

D. E. Jennings,[1] C. A. Nixon,[1,2] A. Jolly,[3] B. Bézard,[4] A. Coustenis,[4] S. Vinatier,[4] P. G. J. Irwin,[5]
N. A. Teanby,[5] P. N. Romani,[1] R. K. Achterberg,[1,2] and F. M. Flasar[1]

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ABSTRACT

This Letter reports the first detection of the three ^{13}C isotopologues of HC_3N on Titan, from *Cassini* Composite Infrared Spectrometer (CIRS) infrared spectra. The data are limb spectra taken at latitudes N54°–N69° in 2006 and 2007 when HC_3N was enhanced in the north. Using a new line list for the ν_5 bands of all isotopologues, we have modeled the isolated emission of $H^{13}CCCN$ at 658.7 cm^{-1} and both $HC^{13}CCN$ and $HCC^{13}CN$ at 663.0 cm^{-1}, which are blended with the *Q*-branch of HC_3N at 663.3 cm^{-1} at the resolution of CIRS (0.5 cm^{-1}) and detectable as an increase in the intensity of the low-frequency wing. Using the resolved pair $H^{13}CCCN$ /HC_3N we find $^{12}C/^{13}C = 79 \pm 17$, in line with other measurements on Titan from *Cassini* and *Huygens*.

Subject headings: infrared: solar system — planets and satellites: formation —
planets and satellites: individual (Titan) — radiative transfer

1. INTRODUCTION

HC_3N was first detected in Titan's stratosphere by the *Voyager* IRIS infrared spectrometer (Kunde et al. 1981). It is produced in the upper atmosphere by the substitution of the CN group—derived from HCN photolysis—for H in C_2H_2 and C_2H_4. IRIS detected two bands of HC_3N: the strong ν_5 at 663 cm^{-1} and weaker ν_6 at 500 cm^{-1}. Subsequent reanalysis of the IRIS data by Coustenis & Bézard (1995) found that HC_3N, like HCN, C_4H_2, and C_3H_4, showed a dramatic increase of at least an order of magnitude above N50° at the *Voyager* epoch (northern spring equinox).

More recently, the Composite Infrared Spectrometer (CIRS; Kunde et al. 1996; Flasar et al. 2004) onboard *Cassini* has returned infrared spectra of Titan obtained during more than 40 close flybys. CIRS has mapped Titan from pole to pole at various spectral resolutions, painting a detailed picture of the trace gas distributions in the northern winter, somewhat earlier than the *Voyager* season. Teanby et al. (2006) analyzed CIRS data at medium (2.5 cm^{-1}) spectral resolution, showing that HC_3N was increasing rapidly above N40°, inside the northern polar vortex. Similarly, Coustenis et al. (2007) measured a 100-fold increase in HC_3N between S65° and N65°. The vertical profile of HC_3N was studied by Teanby et al. (2007) from CIRS limb observations, who found evidence for possible layering at high northern latitudes, perhaps due to haze formation.

CIRS has also detected many isotopologues of trace gases, including $^{13}CH_4$, CH_3D, $^{13}CH_3D$, $^{13}C^{12}CH_2$, $^{13}C^{12}CH_6$, $H^{13}CN$, $HC^{15}N$, and C_2HD (Bézard et al. 2007; Vinatier et al. 2007b; Coustenis et al. 2008; Nixon et al. 2008a). Recently, Nixon et al. (2008b) have reported the first detection of the isotopologues $^{13}CO_2$ and (tentatively) $CO^{18}O$ on Titan. In this Letter we report CIRS observations of infrared emissions from ^{13}C-substituted HC_3N, which we modeled using recent spectral analysis by Jolly et al. (2007). As ^{13}C can be substituted into three nondegenerate bonding positions, the emissions arising from the three isotopomers differ spectrally. In this Letter we focus on the HC−C bending mode (ν_5), centered at 658.7 cm^{-1} for the $H^{13}CCCN$ isotopomer and centered at 663.0 cm^{-1} for both $HC^{13}CCN$ and $HCC^{13}CN$. The latter two isotopomers are blended with the HC_3N emission at 663.3 cm^{-1} at maximum CIRS resolution (0.5 cm^{-1}). Note that the ν_5 band of $HCCC^{15}N$ at 663.3 cm^{-1} is completely coincident with the main band of HC_3N at our resolution, making its detection impossible.

The amount of ^{13}C relative to ^{12}C in Titan's HC_3N provides an indication of the degree of carbon isotope fractionation in the production of secondary nitriles, whereas the overall $^{12}C/^{13}C$ on Titan (approximately the CH_4 value) is a result of primordial solar system isotopic abundances, Titan accretion processes, and subsequent carbon loss from the atmosphere. Therefore, any variations between species may shed light on current atmospheric processing.

2. OBSERVATIONS

CIRS consists of two interferometers sharing the same telescope, foreoptics, and scan mechanism: a polarizing interferometer in the far-infrared (10–600 cm^{-1}, 1000–17 μm) and a Michelson type in the mid-infrared (600–1500 cm^{-1}, 17–7 μm). While the far-infrared focal plane (FP1) has a single 4 mrad circular field of view (FOV), the mid-infrared focal plane consists of two parallel 1 × 10 detector arrays: FP3 (600–1100 cm^{-1}) and FP4 (1000–1500 cm^{-1}). Spectral resolution is variable between 15 (low) and 0.5 (high) cm^{-1} (for further details, see Kunde et al. 1996; Flasar et al. 2004).

We have focused here on the analysis of three similar limb observations at northern latitudes, which consist of long-duration dwells with the 1 × 10 arrays placed perpendicular to Titan's limb, to gain a vertical composition profile. The highest spectral resolution (0.5 cm^{-1}) is used to increase sensitivity to trace gases and isotopes. Each observation (3.5–4 hr) samples only a single latitude, with the arrays centered at two different tangent heights for ~90–120 minutes at each position to gain a complete section from 0 to 500 km and with overlap between the two positions.

We selected three northern latitude observations for analysis—N54°, N61°, and N69°—where the abundance of the short-lived HC_3N is greatly enhanced at the present epoch (northern winter), probably due to downward advection in the descending

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[1] NASA Goddard Space Flight Center, Code 693, Greenbelt, MD 20771.

[2] University of Maryland, College Park, MD 20742; conor.a.nixon@nasa.gov.

[3] LISA, CNRS, Universités de Paris 12 and Paris 7, 94010 Créteil Cedex, France.

[4] LESIA, Observatoire de Paris, 5 Place Jules Janssen, 92195 Meudon Cedex, France.

[5] Atmospheric, Oceanic and Planetary Physics, University of Oxford, Clarendon Laboratory, Parks Road, Oxford OX1 3PU, UK.

TABLE 1

Observations and Results

Flybys	Date	Latitude (deg)	VMR Range[a] (km)	$^{12}C/^{13}C$ Altitude[b] (km)	N_{spec}	$^{12}C/^{13}C$ (659 cm^{-1})
T10	2006 Jan 15	54	145–272	146	126	91 ± 51
T19	2006 Oct 9	61	152–270	152	92	63 ± 22
T35	2007 Aug 31	69	151–282	150	67	102 ± 29
Mean						79 ± 17

[a] Altitude range used to determine vertical gas and temperature profiles.

[b] Approximate peak value of final average used to find scaled profiles for isotopic ratios.

branch of a planetary stratospheric circulation cell (Hourdin et al. 2004; Teanby et al. 2008a, 2008b). This enhances the S/N for HC_3N, especially important for the weak isotopologues. See Table 1 for details.

3. DATA ANALYSIS

The data analysis at each latitude proceeded in three stages: (1) the vertical temperature profile was determined by modeling the ν_4 band of CH_4, assuming a uniform mole fraction of 1.4%; (2) the volume mixing ratio (VMR) profiles for relevant trace gas species (major isotopologues only) was inferred based on the measured temperatures; and (3) the VMR profiles were scaled to represent isotopologue species, and the abundances were determined, enabling the measurement of $^{12}C/^{13}C$.

The first step was to create vertically binned spectra for FP4 at each latitude, where the bin boundaries were set by a cluster analysis technique. This method grouped together spectra whose tangent altitude at pixel center differed by less than half of the ≃40 km field of view (FOV). Altitudes were corrected for differences between *Cassini* standard pointing values and self-consistent retrieval altitudes, as described in Vinatier et al. (2007a). Ten spectra with corrected mean tangent altitudes (at pixel center) in the range 150–300 km were then selected for modeling, using the spectral range 1225–1325 cm^{-1}, covering the *P*- and *Q*-branches of CH_4. The spectral modeling method has been described in Nixon et al. (2008b) and uses the Nemesis computer code to generate synthetic spectra and to retrieve best-fit model parameters (Irwin et al. 2008): the main difference here is that we simultaneously inverted multiple spectra over a range of altitudes to derive a temperature profile from ∼1.0 to 0.1 bar.

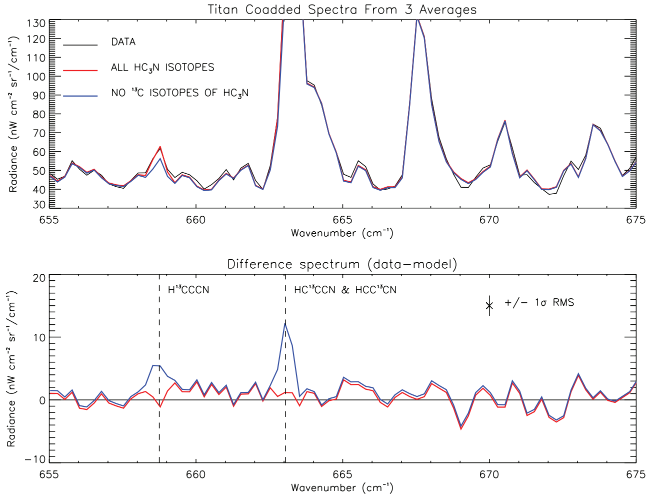

Fig. 1.—*Top:* Mean observed spectrum from weighted average of data sets in Table 1 (N54°–N69°, 125–175 km). *Bottom:* residual emission after subtracting two model fits from the data (weighted mean over three latitudes): one with no ^{13}C isotopologue band opacity, and the other with isotopic species at best-fit abundances.

We then used the altitude binning technique to average spectra for FP3 in the same vertical range, selecting a spectral range from 655 to 675 cm^{-1}. This exhibits emissions from the C_2H_2 ν_5 *P*-branch, HCN ν_2 *P*-branch, CO_2 ν_2 band, C_6H_6 ν_4 band, and ν_5 band of HC_3N. Beginning with VMR profiles that were constant with height in the stratosphere and the retrieved temperature profile from the previous stage, we derived vertical gas profiles that best fit the data. This step was needed because the VMR profiles of trace gases, especially the short-lived HC_3N, show significant vertical gradients in the north (Teanby et al. 2007). In addition to the gas vertical profiles, a haze absorber vertical profile was also determined, based on the optical properties of lab tholin (Khare et al. 1984).

Finally, we created a larger spectral average at each latitude over an altitude range 125–175 km, with a mean altitude of ∼150 km, to increase the S/N for the weak emissions from the HC_3N isotopologues. Using the retrieved vertical profiles of the trace gases, we then created profiles for the isotopic species—^{13}C-HC_3N (treated in the model as one gas, with three ν_5 bands), $^{13}C^{12}CH_2$, and $CO^{18}O$—by scaling the retrieved profiles of the major isotopologues by factors of 0.01213, 0.02430, and 0.004. All trace gas profiles (major and minor isotopologues) were then varied linearly in VMR to achieve an optimal spectral fit.

Note that, in addition to the spectral data of Nixon et al. (2008b), we compiled further *k*-tables from new line lists for the ν_5 bands of all three ^{13}C and the ^{15}N isotologues of HC_3N. These were derived by us from the recent spectral analysis of Jolly et al. (2007) on the ν_5 band of the main isotope of HC_3N.

4. RESULTS AND DISCUSSION

Figure 1 (*upper panel*) shows the overall mean spectrum—weighted by the number of spectra in each final latitude average—compared to two model calculations: one with (*red*) and one without (*blue*) the ^{13}C isotopologues of HC_3N in the model. The lower plot shows the residual (data − model) for each of the two calculations, clearly showing (*in blue*) the *Q*-branch emissions of the isotopologues: $H^{13}CCCN$ at 658.7 cm^{-1} and also $HC^{13}CCN$ and $HCC^{13}CN$ at 663.0 cm^{-1}. The measured line peak radiances are 6.5 nW cm^{-2} sr^{-1} $(cm^{-1})^{-1}$ (4 σ) and 11.0 nW cm^{-2} sr^{-1} $(cm^{-1})^{-1}$ (7 σ) respectively, where σ is the estimated standard deviation of random noise. As expected, the emission in the second feature is larger than the first, because two different isomers are contributing rather than one.

However, measuring the $^{12}C/^{13}C$ ratio using all three isotopologue bands simultaneously proved unreliable. After various tests, we found that the reason comes from the 0.5 cm^{-1} CIRS resolution that does not allow us to resolve the 663.0 cm^{-1}

isotopologue bands from the much stronger HC_3N main emission at 663.3 cm^{-1}. The determination of the $^{12}C/^{13}C$ ratio using the 663.0 cm^{-1} isotopic bands turned out to be impossible as any change in the isotopic ratio can be offset by a tiny change in the HC_3N abundance. We thereafter used only the 658.7 cm^{-1} isotopic band to derive the $^{12}C/^{13}C$ ratio from the individual spectral selections.

The mean $^{12}C/^{13}C$ ratio at 658.7 cm^{-1} over all three latitudes is 79 ± 17, derived by weighting the individual values by the reciprocal of the variance (Bevington 1969). This is consistent with $^{12}C/^{13}C$ derived for CH_4 by the *Huygens Probe* mass spectrometer: 82.3 ± 1 (GCMS; Niemann et al. 2005) and also with the terrestrial standard (88.9). Sada et al. (1996) have measured $^{12}C/^{13}C = 99^{+43}_{-23}$ in Saturn's C_2H_6 and derived a weighted average for the outer planets of 88 ± 7, based on nine hydrocarbon measurements for Jupiter, Saturn, and Neptune. HC_3N is produced by the substitution of the cyanide radical ($-C{\equiv}N$), produced by photolysis of HCN, in C_2H_2, and therefore we expect the $^{12}C/^{13}C$ ratio to be comparable to that of these two progenitors. The $^{12}C/^{13}C$ ratio in HCN has been measured in the submillimeter at 70–120 (Hidayat et al. 1997) and 88–157 (Gurwell 2004), and also in the mid-infrared by CIRS at 75 ± 12 (Vinatier et al. 2007b). Our mean value is in good agreement with all these measurements. The $^{12}C/^{13}C$ ratio in C_2H_2 was measured by Nixon et al. (2008a) as 85 ± 3, compatible with the CIRS HCN $^{12}C/^{13}C$, and the mean value for HC_3N.

There is evidence at present for a slight enrichment (~8%) in $^{12}C/^{13}C$ versus terrestrial (~89), most notably in the GCMS measurements of CH_4 where the S/N is highest. In the other species, which largely derive their carbon from photolysis of CH_4, we expect similar ratios although the accuracy is not yet sufficient to distinguish strongly from a terrestrial value. In the future, higher spectral resolution measurements than CIRS can resolve the 663.0–663.5 cm^{-1} region and measure $HCC^{13}CN$, in principle distinguishing between carbon isotopic ratios in the cyanide group (CN) originating from HCN and in the acetyl group (C_2H) from C_2H_2 and providing further constraints on photochemistry. The $HCCC^{15}N$ isotopologue might also be more easily detected in the ν_6 band near 500 cm^{-1}, where the isotopic line shift is ~1.2 cm^{-1} (Bénilan et al. 2006), permitting measurement of $HC_3^{14}N/HC_3^{15}N$.

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