14N/15N Isotopic Ratio in CH3CN of Titan’s Atmosphere Measured with ALMA

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Abstract

The nitriles present in the atmosphere of Titan can be expected to exhibit different 14N/15N values depending on their production processes, primarily because of the various N2 dissociation processes induced by different sources such as ultraviolet radiation, magnetospheric electrons, and Galactic cosmic rays. For CH3CN, one photochemical model predicted a 14N/15N value of 120–130 in the lower stratosphere. This is much higher than that for HCN and HC3N, ~67–94. By analyzing archival data obtained by the Atacama Large Millimeter/submillimeter Array, we successfully detected submillimeter rotational transitions of CH3C15N (J = 19–18) located in the 338 GHz band in Titan’s atmospheric spectra. By comparing those observations with the simultaneously observed CH3CN (J = 19–18) lines in the 349 GHz band, which probe from 160 to ~400 km altitude, we then derived 14N/15N in CH3CN as 125±144. Although the range of the derived value shows insufficient accuracy due to limitations on data quality, the best-fit value suggests that 14N/15N for CH3CN is higher than values that have previously been observed and theoretically predicted for HCN and HC3N. This may be explained by the different N2 dissociation sources according to altitude, as suggested by a recent photochemical model.

Unified Astronomy Thesaurus concepts: Planetary atmospheres (1244); Submillimeter astronomy (1647)

1. Introduction

The presence of complex nitriles has been seen as one of the key features of Titan’s atmosphere since a millimeter emission spectrum of the Titan’s most abundant nitrile, HCN, was obtained in 1986 by the Institut de Radioastronomie Millimétrique using a 30 m single-dish telescope (Paubert et al. 1987). Since that time, other nitriles such as HC3N, CH2CN, HNC, and C2H2CN have been discovered by space- and ground-based millimeter and submillimeter observations (Marten et al. 2002; Moreno et al. 2011; Cordiner et al. 2015a). It is currently thought that the production of the above-described nitriles starts with the dissociation of N2 into N-atoms, which is induced by ultraviolet (UV) radiation, magnetospheric electrons (ME), and Galactic cosmic rays (GCRs). Recently, Loison et al. (2015) developed a neutral and ion chemistry model with which they successfully reproduced the observed vertical profiles of nitriles. According to their model, the main production path of HCN is as follows: N(5S) + CH3 → HCN + H, H2CN + H → HCN + H2, where N(5S) is a ground-state N-atom. In turn, N(2D), an excited-state N-atom, easily reacts with CH3, which is the second most abundant species on Titan, and produces CH2NH. CH2NH is lost by photodissociation and produces H2CN, which leads to HCN production. Once HCN is formed, its photolysis produces CN radicals, which subsequently react with C2H2 to produce HC3N. Here, it is noted that the production process for HCN, which is an isomer of HCN, is similar to that for HCN. HNC is a minor product of the reaction H2CN + H.

The production path for CH3CN is expected to be different from that for HCN and its daughter species. Loison et al. (2015) suggested that the main production path for CH3CN is N(5S) + C2H3 → CH3CN, CH3CN + H + M → CH2CN. CH2CN produces C2H2CN by reacting with abundant CH3 radicals, and it is expected that the production of the C2H2 radical occurs only in high-pressure (low-altitude) regions (Loison et al. 2015). At such low altitudes, photodissociation of N2 hardly ever occurs. Instead, it is considered likely that the production of N(5S) at those altitudes can be attributed to GCR-induced N2 dissociation. A recent model by Dobrijevic & Loison (2018) showed that, below 600 km, the production of N(5S) is dominated by GCR-induced dissociation, not by UV or MEs. Thus, the production of CH3CN and C2H2CN can be expected to continue below 600 km.

As mentioned above, the different N2 dissociation processes lead to complex nitrogen compositions and chemistry. This is important because observations of the nitrogen isotopic ratio 14N/15N can be of use when evaluating theoretical models of Titan’s atmospheric chemistry. Dobrijevic & Loison (2018) predicted that 14N/15N measured for the nitriles would change significantly depending on their production processes, in particular the dissociation process of N2. Here, it should be noted that although dissociation due to GCR does not produce any isotopic fractionation, the same is not true for dissociation due to UV and MEs. Due to the self-shielding nature of UV, N14N is not dissociated effectively in the upper stratosphere, whereas MEs dissociate N14N ∼ 10 times more effectively than UV (Dobrijevic & Loison 2018). In turn, in the case of N15N, UV dissociation is stronger than that of MEs because of less self-shielding.

The photochemical model of Dobrijevic & Loison (2018) suggested that CH3CN and C2H2CN have large differences in 14N/15N values compared with those for HCN and HC3N because of their production path differences. More specifically, the modeled 14N/15N values for CH3CN and C2H2CN are ∼80 at high altitudes (∼800 km) and increase to ∼120 in the lower stratosphere (∼200 km), while those for HCN and HC3N are expected to be relatively constant at ∼80 at altitudes below 800 km. These modeled values for HCN and HC3N are in good agreement with previous observation results of 94 ± 13 (Gurwell 2004) and 72.2 ± 2.2 (Moler et al. 2016) for HCN, and 67 ± 14 (Cordiner et al. 2018) for HC3N. Interestingly, there is another photochemical model showing different 14N/15N values for nitriles. Vuitton et al. (2019)
modeled nitrile chemistry including isotopic fractionation processes, which indicated that $^{14}\text{N}/^{15}\text{N}$ for CH$_3$CN at high altitude (>1000 km) is smaller than that of HCN and HC$_3$N because they proposed that CH$_3$CN is produced from N(2D), which is enriched in $^{15}$N. In turn, in the lower stratosphere (at 200 km), three nitriles are expected to exhibit similar $^{14}\text{N}/^{15}\text{N}$ values of $\sim$55 because non-fractionated N-atoms produced by GCR collision with N$_2$ homogenize $^{14}\text{N}/^{15}\text{N}$ in nitriles via recycling processes.

As mentioned above, GCR influx is a possible candidate that affects the composition of trace species on Titan. To constrain and evaluate the effect of GCR influx, observational derivations of $^{14}\text{N}/^{15}\text{N}$ for CH$_3$CN are crucial. Recently, Palmer et al. (2017) detected a CH$_3$C$^{15}$N signal in the submillimeter spectra taken by the Atacama Large Millimeter/submillimeter Array (ALMA), and reported $^{15}$N/$^{15}$N in CH$_3$CN as 89 ± 5. In the analysis, the CH$_3$CN abundance profile was assumed to be the same as a reference profile derived in Marten et al. (2002), which means that the respective observations of CH$_3$C$^{15}$N and CH$_3$CN were conducted at different respective epochs of 2014 and 1998, with significantly different spatial resolutions. In addition, while the detail of the observation has not yet been published, Cordier et al. (2015b) also analyzed ALMA data and reported a low $^{14}\text{N}/^{15}\text{N}$ value in CH$_3$CN as 58 ± 8, which is consistent with that modeled by Vuitton et al. (2019).

It should be noted that a similar GCR-induced production of trace species and change in brightness have also been proposed for Neptune (Lellouch 1994; Aplin & Harrison 2016). From the viewpoint of planetary science, an understanding of the effects of GCRs on atmospheric compositions is important because the process may be universally applicable to planets.

In this study, we attempt to measure the $^{14}\text{N}/^{15}\text{N}$ value for CH$_3$CN from simultaneously obtained CH$_3$CN and CH$_3$C$^{15}$N data. Both the atmospheric structure and the abundances of nitriles on Titan, including CH$_3$CN, are known to exhibit seasonal and spatial variation. In addition, due to the limited coverage of the data sampling in the $uv$ plane, the synthesized beam of the radio interferometer has an elliptical shape and varies with the time of the observations. Therefore, for the precise determination of $^{14}\text{N}/^{15}\text{N}$ in CH$_3$CN, the two isotopologues are to be recorded quasi-simultaneously with a common synthesized beam.

2. Data Analysis

2.1. Extracting Titan Data from the ALMA Archive

The atmosphere of Titan is known to have seasonal variations in its thermal structure (e.g., Achterberg et al. 2008; Vinatier et al. 2010; Coustenis et al. 2013, 2018; Thelen et al. 2018). The distribution of CH$_3$CN within Titan’s atmosphere also shows strong seasonal variations and spatial inhomogeneity (e.g., Cordiner et al. 2015a; Lai et al. 2017; Thelen et al. 2019). Therefore, researchers must always be careful when interpreting an isotopic ratio if the values were derived from the data on two isotopologues taken at different observation dates and/or with different spatial resolutions. Keeping this point in mind, we searched the publicly released ALMA archive to identify the most favorable data for analyzing CH$_3$CN and CH$_3$C$^{15}$N.

CH$_3$CN and CH$_3$C$^{15}$N have a large number of spectral lines with a variety of line strengths at millimeter and submillimeter wavelengths. Data in the ALMA archive contain Titan as a science target and also as a flux calibrator. Accordingly, we began with a data search conducted among spectral cubes (spatial maps having spectral dimensions). However, since spectral cubes for use as calibration data had not previously been prepared in the archive, it was necessary for us to reduce them from raw visibility data. The calibration was done using the QA-2 pipeline script produced by the Analysis Utilities given by the ALMA observatory. In addition, we have removed the spectral line flagging process in the script to preserve Titan’s atmospheric spectra. Calibrated data sets for Titan were split into spectral windows (SPWs), and their line-of-sight Doppler-shift velocity values were corrected. The continuum and line emissions were separated in the $uv$ plane. This process was needed to improve the dynamic range of the synthesized images, because our target spectral line features are weak. At the same time, synthesis images including the continuum emission are also required since we need to calibrate the flux density of Titan with respect to simulated spectra from our radiative transfer model (see Section 2.2). Imaging was performed with the CLEAN method with oscllean mode to produce a 320 × 320 pixel image with 0″025 spacing. A CLEAN mask with 1″5 diameter circle was placed at the center of Titan’s disk.

By examining all the CLEANed Titan images in the ALMA archival data, we successfully detected spectral features of CH$_3$C$^{15}$N in several data sets. We found that the data of ObsID 2013.1.00033.S contained two SPWs that include rotational transitions of CH$_3$C$^{15}$N ($J = 19–18$) in the range 338.88–338.92 GHz and CH$_3$CN ($J = 19–18$) in the range 349.21–349.45 GHz, respectively, in one observation performed on 2015 April 29. Note that both data were obtained for the purpose of flux and amplitude calibration, and CH$_3$CN ($J = 19–18$) was flagged in the originally archived data for the precise measurement of Titan’s continuum emission. The observation time was 157 s, with seven observation scans taken at 6.05 s intervals. The center frequencies of SPWs for CH$_3$C$^{15}$N and CH$_3$CN were 337.995 and 350.116 GHz, respectively. Since the total bandwidth was 1874.956 MHz and the number of channels was 3840, the spectral resolution was 488.270 kHz. The number of 12 m antennas used for the observation was 39. The quasar J2056–4714 was used for bandpass and phase calibration. The synthesis beam size was 1″19 × 0″62 (position angle = −70°3). The apparent disk diameter (2575 km) of Titan was 0″78 at the observed time, and the sub-Earth latitude was 24°37 N.

Figure 1 shows an integrated intensity map for a CH$_3$CN line of $J = 19(3)–18(3)$, which is the strongest line in the $J = 19–18$ band. Here it can be seen that the intensity peak is located in the northern mid-latitude region, which is consistent with past observations of the seasonal behavior of this species (Thelen et al. 2019). The thick Titan atmosphere creates significant limb brightening, and the emission originally extends outside the 0″78 diameter disk. Moreover, the limb emission is spatially spread due to the synthesized beam. In order to collect such extended emission, we averaged the spectra within a region that included the Titan atmosphere up to an altitude of 1200 km (≈1″15 diameter disk area, which is indicated by a dashed line in Figure 1). The disk-averaged spectra of both isotopologues are displayed in Figures 3(a) and 4(a).
2.2. Radiative Transfer Analysis

Next, we calculated the radiative transfer of atmospheric emissions from Titan. Our radiative transfer model is based on the one used in Rengel et al. (2014), which consists of a line-by-line calculation using spherically uniform atmospheric layers. The atmosphere from the surface up to 900 km is divided into 240 layers (2–10 km depth). For the temperature profile, we referred to a recent work by Thelen et al. (2018), in which a disk-averaged temperature profile was retrieved from ALMA archived data observed on 2015 June 27 (∼2 months after the observation date of the data used in this study) (Figure 2). An a priori profile for CH$_3$CN was taken from Marten et al. (2002). Pencil-beam synthesis spectra were calculated under various emission angle conditions, including the limb-viewing geometry, and then convolved with an elliptic beam of the CLEANed image. The flux density for the observed spectrum was then calibrated against the continuum brightness of the forward model spectrum.

A vertical profile of CH$_3$CN was retrieved from the $J = 19$–18 transitions at 349.21–349.45 GHz. Figure 3(a) shows the observed and best-fit spectra of CH$_3$CN. The a priori and retrieved vertical profiles are shown in Figure 3(b). Since the goal of this paper is to discuss the $^{14}$N/$^{15}$N value for CH$_3$CN, we will not discuss the result of the retrieved CH$_3$CN profile in detail, but we briefly compared it with the work by Thelen et al. (2019), which retrieved a CH$_3$CN profile from data taken on 2015 May 19. Our disk-averaged CH$_3$CN profile shows an increase in the volume mixing ratio at the middle stratosphere (∼300 km) and a decrease at ∼360–420 km. Such a vertical oscillation is also seen (although not fully consistent) in the result of the northern hemispheric CH$_3$CN profile in Thelen et al. (2019).

The retrieved CH$_3$CN profile was used to constrain the CH$_3$C$^{15}$N abundance by fitting the observed spectrum with a forward model spectrum. A vertically constant isotopic ratio is assumed in this study. The reduced $\chi^2$ values were calculated as a function of the scaling factor of CH$_3$C$^{15}$N with respect to the CH$_3$CN volume mixing ratio. Figure 4(a) shows the best-fit spectrum. Three CH$_3$C$^{15}$N lines are clearly detected in the observed SPW, and $\chi^2$ values were calculated using the data within a spectral range of ±16 MHz around the line with the best signal-to-noise ratio at 338.882 GHz. The best-fit (the minimum of $\chi^2$) was obtained when the scaling factor was 0.0079, which corresponds to a $^{14}$N/$^{15}$N value of 125. It is noted that this isotopic ratio also reproduces the other two CH$_3$C$^{15}$N lines that are not used in the fitting analysis. The fitting uncertainty was estimated from the range of
wheren = 1.02, where \( cD \) is the difference from the minimum \( c2 \) value. The corresponding uncertainty range was obtained as \( \frac{14N}{15N} = 81–270 \) (Figure 4(b)). The derived error range includes the previously reported \( \frac{14N}{15N} \) value of 89 \( \pm 5 \) (Palmer et al. 2017).

3. Discussion

3.1. Caveat of the Data Analysis

Contrary to the model proposed by Dobrijevic & Loison (2018), which suggests the presence of a large gradient in the \( \frac{14N}{15N} \) isotopic ratio with altitude, we have assumed a vertically constant isotopic ratio in this study. The quality of the \( CH3CN \) spectrum used in this study is not sufficient to make it possible to retrieve vertically resolved information. This is a caveat of the current analysis.

In order to check the information on the altitudes at which the observed spectra are sensitive, Jacobians for \( CH3CN \) and \( CH3C5N2 \) are shown in Figure 5. A Jacobian is a matrix of partial derivatives of the spectral radiance at each frequency with respect to the volume mixing ratios of \( CH3CN \) at each altitude, which express the sensitivity to the species at that altitude. The plotted Jacobians were calculated using the retrieved \( CH3CN \) profile (as shown in Figure 3(b)) and the best-fit \( \frac{14N}{15N} \) value. It is shown that the emission at the line centers of \( CH3CN \) has sensitivity to \( CH3CN \) at altitudes from 160 to \( \sim400 \) km, with the peak weight located at \( \sim300 \) km. The probing altitude shifts downward as the frequency moves further from the line center. The Jacobian of \( CH3C5N2 \) shows weaker sensitivity over a narrower altitude range than that of \( CH3CN \), which is due to the weaker line opacity of \( CH3C5N2 \). Because we used not only the center but also the wings of the line in the \( CH3CN \) spectra for the retrieval analysis, our derived \( CH3CN \) profile is also sensitive to the lower altitudes to which the \( CH3C5N2 \) line is sensitive. In other words, the sensitive altitude ranges of \( CH3CN \) and \( CH3C5N2 \) are not completely separated in this study.
3.2. Impact of the Assumed Temperature Profile

One of the potential error sources in this study is the uncertainty in the temperature profile used in the radiative transfer calculation. We tested different temperature profiles for the $^{14}\text{N}/^{15}\text{N}$ derivation. Thelen et al. (2018) derived not only a disk-averaged temperature profile, but also temperature profiles representing the northern and southern hemispheres of Titan (Figure 2). Considering the fact that CH$_3$CN is enhanced in the northern hemisphere, as shown in Figure 1, the use of the northern hemispheric temperature profile provides an alternative choice when selecting a temperature profile for analyzing the CH$_3$CN spectra. If we use the northern hemispheric temperature profile of Thelen et al. (2018), the best-fit $^{14}\text{N}/^{15}\text{N}$ in CH$_3$CN was 129, which is not very different from that when using the disk-averaged temperature profile. Thus, these results allow us to conclude that the uncertainty that arises from the temperature profile used in this study is not prohibitive.

3.3. Comparisons with the Model and Future Perspectives

The best-fit $^{14}\text{N}/^{15}\text{N}$ value for CH$_3$CN, which is 125, falls within the range of values obtained in the theoretical study of Dobrijevic & Loison (2018) (derived as 70–170 at 200 km, as the result of the Monte Carlo simulation). As mentioned in Section 1, CH$_3$CN is expected to have two possible N-atom origins: UV- and GCR-induced dissociation. Dobrijevic & Loison (2018) simulated the contribution of these two processes to $^{14}\text{N}/^{15}\text{N}$ for CH$_3$CN, and found that $^{14}\text{N}/^{15}\text{N}$ has two possible peak values, 90 and 160 (at 200 km), which correspond to the UV and GCR origin scenarios, respectively. However, due to the limitation on data quality, the $^{14}\text{N}/^{15}\text{N}$ value derived in this study is not sufficiently accurate to clearly differentiate between these two possible $^{14}\text{N}/^{15}\text{N}$ scenarios. In contrast to CH$_3$CN, both HCN and HC$_3$N were expected to exhibit low $^{14}\text{N}/^{15}\text{N}$ value of 79.5 ± 6.5 and 79.6 ± 6.5, respectively, in the model. Our derived best-fit value of $^{14}\text{N}/^{15}\text{N}$ for CH$_3$CN is inconsistent with these, which supports the model’s prediction of the different N$_2$ dissociation sources among these nitriles.

To obtain further observational constraints, a dedicated observation of CH$_3$CN/CH$_3$C$^{15}$N with better sensitivity is required. In addition, derivation of a vertical profile of $^{14}\text{N}/^{15}\text{N}$ for CH$_3$CN could provide a good evaluation of the model because Dobrijevic & Loison (2018) predicted that the vertical distribution of $^{14}\text{N}/^{15}\text{N}$ might possibly exhibit a large gradient. Additionally, both the temporal and spatial variations of $^{14}\text{N}/^{15}\text{N}$ derived by additional observations will be useful for facilitating better understanding of the contributions of production processes in different environments (different UV conditions, for example).

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References
Achterberg, R. K., Conrath, B. J., Gierasch, P. J., Flasar, F. M., & Nixon, C. A. 2008, Icar, 194, 263
Aplin, K. L., & Harrison, R. G. 2016, NatCo, 7, 11976
Cordiner, M. A., Nixon, C. A., Charnley, S. B., et al. 2018, ApJL, 859, L15
Cordiner, M. A., Palmer, M. Y., Nixon, C. A., et al. 2015a, ApJL, 800, L14
Cordiner, M. A., Palmer, M. Y., Nixon, C. A., et al. 2015b, AAS/DPS Meeting, 47, 205.03
Coustenis, A., Bampasidis, G., Achterberg, R. K., et al. 2013, ApJ, 779, 177
Coustenis, A., Jennings, D. E., Achterberg, R. K., et al. 2018, ApJL, 854, L30
Dobrijevic, M., & Loison, J. C. 2018, Icar, 307, 371
Gurwell, M. a. 2004, ApJL, 616, L7
Lai, J. C. Y., Cordiner, M. A., Nixon, C. A., et al. 2017, AJ, 154, 206
Lellouch, E. 1994, Icar, 108, 112
Loison, J. C., Hebrard, E., Dobrijevic, M., et al. 2015, Icar, 247, 218
Marten, A., Hidayat, T., Biraude, Y., & Moreno, R. 2002, Icar, 158, 532
Molter, E. M., Nixon, C. A., Cordiner, M. A., et al. 2016, AJ, 152, 42
Moëro, R., Lellouch, E., Lara, L. M., et al. 2011, A&A, 536, L12
Palmer, M. Y., Cordiner, M. A., Nixon, C. A., et al. 2017, SciA, 3, e1700022
Paubert, G., Marten, A., Rosolen, C., Gautier, D., & Courtin, R. 1987, BAAS, 19, 633
Rengel, M., Sagawa, H., Hartogh, P., et al. 2014, A&A, 561, A4
Thelen, A. E., Nixon, C., Chanover, N., et al. 2019, Icar, 319, 417
Thelen, A. E., Nixon, C. A., Chanover, N. J., et al. 2018, Icar, 307, 380
Vinatier, S., Bézard, B., Nixon, C. a., et al. 2010, Icar, 205, 559
Vuitton, V., Yelle, R. V., Klippenstein, S. J., Hörst, S. M., & Lavvas, P. 2019, Icar, 324, 120