ALMA DETECTION OF HYDROGEN CYANIDE AND CARBON MONOXIDE IN THE ATMOSPHERE OF SATURN

RESEARCH ARTICLE

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ABSTRACT

The hydrogen cyanide (HCN) molecule in the planetary atmosphere is key to the formation of building blocks of life. We present the spectroscopic detection of the rotational molecular line of nitrile species hydrogen cyanide (HCN) in the atmosphere of Saturn using the archival data of the Atacama Large Millimeter/Submillimeter Array (ALMA) in band 7 observation. The strong rotational emission line of HCN is detected at frequency $\nu = 354.505$ GHz (>4$\sigma$ statistical significance). We also detect the rotational emission line of carbon monoxide (CO) at frequency $\nu = 345.795$ GHz. The statistical column density of hydrogen cyanide and carbon monoxide emission line is $N(\text{HCN}) \sim 2.42 \times 10^{16}$ cm$^{-2}$ and $N(\text{CO}) \sim 5.82 \times 10^{17}$ cm$^{-2}$. The abundance of HCN and CO in the atmosphere of Saturn relative to the H$_2$ is estimated to be $f(\text{HCN}) \sim 1.02 \times 10^{-9}$ and $f(\text{CO}) \sim 2.42 \times 10^{-8}$. We discussed possible chemical pathways to the formation of the detected nitrile gas HCN in the atmosphere of Saturn.

Keywords: planets and satellites: individual: Saturn – planets and satellites: atmospheres – Radio lines: planetary systems – Astrochemistry – Astrobiology

1 Introduction

In the stratosphere of Saturn, the hydrocarbon species are formed due to the photochemistry of methane (Encrenaz, 2004). The ISO-SWS instrument detected CH$_3$C$_2$H, C$_4$H$_2$, C$_6$H$_6$ and CH$_3$ in the stratosphere of Saturn (Graauw et al., 1997). The maximum numbers of hydrocarbon species are found in the stratosphere of Saturn compared to the other giant planets. In the upper stratosphere of Saturn, CH, CH$_2$, and CH$_3$ are produced due to the photodissociation of methane (Fouchet et al., 2009). In the stratosphere of Saturn, the hydrocarbon species C$_2$H$_6$ and C$_2$H$_2$ are detected in the UV and infrared wavelength (Moos & Clarke, 1979; Tokunaga et al., 1975).

In our solar system, the discovery of prebiotic molecules is particularly interesting in the outer planets. The Voyager mission first detected the hydrogen cyanide (HCN) gas on Saturn moon Titan (Hanel et al., 1981). The HCN molecule could play an important role in the formation of outer planet atmospheres. In the atmosphere of Saturn, Tokunaga et al. (1981) did not find any emission and absorption feature of HCN due to poor signal to noise ratio. Tokunaga et al. (1981) proposed the mixing ratio of HCN in the atmosphere of Saturn is $7 \times 10^{-9}$. Using the photochemical calculation, Kaye & Goldman (1983) find the mixing ratio of HCN is $5 \times 10^{-10}$. The observation of HCN molecules in Saturn at high spectral resolution is very interesting. Using the heterodyne technique, the resolving power of the HCN line would be at least $10^6$ and the four strongest HCN rotational lines lie between 800 $\mu$m and 3 mm. In our paper, we present the strong HCN emission line at $\lambda = 0.8$ mm using ALMA.

The H$_2$O and CO$_2$ are detected in the stratosphere of the giant planets and Titan using the Infrared Space Observatory and Spitzer (Feuchtgruber et al., 1997; Coustenis et al., 1998; Lellouch et al., 2002; Burgdorf et al., 2006). The detection of H$_2$O and CO$_2$ are given the evidence of an external source of oxygen in the outer Solar System. This molecule in
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Table 1: Details of ALMA observations and properties of detected species.

| Start date (UT) | Geocentric distance (AU) | Angular diameter (arcsec) | Spectral resolution (kHz) | Integration time (s) | Molecular Species | Frequency (GHz) | Transition (J) | $E_L$ (K) |
|-----------------|--------------------------|---------------------------|--------------------------|----------------------|------------------|----------------|---------------|----------|
| 2018-05-25      | 9.209                    | 17.44                     | 70.56                    | 476.402              | HCN              | 354.505        | 4–3           | 25.521   |
| 2018-05-25      | 9.209                    | 17.44                     | 282.23                   | 476.402              | CO               | 345.795        | 3–2           | 11.535   |

Figure 1: First millimeter-wavelength ALMA image of Saturn at $\lambda = 0.85$ mm with a superior ring system. The synthesized beam size of the image is $0.789'' \times 0.612''$ which denoted as the red small circle in lower-left side of image. The red color position around the north pole indicates the auroral features.

the stratosphere of the giant planets is created due to ring and/or satellite particles, the collision of large comets, and infalling interplanetary dust particles (IDP). The presence of CO in the stratosphere of a giant planet is not implied the external origin of this gas. The CO gas cannot be transported to the stratosphere from the deep hot interior of planets because there is no condensation sink for CO at the tropopause. In the stratosphere of Saturn, the CO is coming from the external source due to the collision of the comet Shoemaker-Levy 9 events (Cavalié et al., 2010).

In this letter, we present the spectroscopic detections of hydrogen cyanide (HCN) and carbon monoxide (CO) in the atmosphere of Saturn using ALMA. In Sect. 2, we briefly describe the observations and data reductions. The result of detection is described in Sect. 3.1. We discuss the possible photochemical pathways to the formation of HCN in Sect. 3.2. The discussion of detection of HCN and CO as well as the formation of other prebiotic molecules in the atmosphere of Saturn is presented in Sect. 4.

2 Observations and data reduction

The Interferometric millimeter data of solar gas planet Saturn was taken from Atacama Large Millimeter/submillimeter Array (ALMA)\(^1\) with 12m system to study the emission of atmospheric gas. The publicly available data of Saturn was observed on 2018-05-25 in which Saturn acts as a flux calibrator, J1751+0939 acts as a bandpass calibrator, and J1832-2039 acts as a phase calibrator. The observation was done with a total of 44 no of antennas.

We used a data processing technique that was very similar to Manna & Pal (2020). The raw data of ALMA in ASDM format was calibrated and bad data was flagged using standard data reduction procedure using Common Astronomy Software Application (CASA 5.1.0)\(^2\). The continuum level was scaled and matched with Butler-JPL-Horizons 2012 flux model within 15% accuracy (Butler, 2012). After the initial data reduction, we separate the target data using MSTRANSFORM task and imaging was performed using TCLEAN task with several numbers of iterations. The Hogbom algorithm, with natural visibility weighting, was used to deconvolve the ALMA point-spread function. The observation

\(^1\)https://almascience.nao.ac.jp/asax/
\(^2\)http://casa.nrao.edu
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Figure 2: Molecular rotational emission spectrum of HCN in the atmosphere of Saturn at the frequency of $\nu = 354.505$ GHz with transition J=4–3 using ALMA band 7 observation. The spectrum was made by integrating the reduced ALMA data cubes from the center of Saturn with 1.1″ circular region. The spectral coverage in the figure is 200 MHz with a total integration time of 476.402 second. In the spectrum, the solid red line corresponds to the best fit model of column density $2.42 \times 10^{16}$ cm$^{-2}$.

details are shown in Tab. 1. In every data cubes, the disk-averaged spectrum was obtained by integrating each channel within a circular region around a core of Saturn, and emission was observed above the $4\sigma$ noise level. On the outside of this field, the flux was found to be negligible. The resultant spectrum was corrected from doppler shift to the rest frame of Saturn using measurement of JPL. The resultant image of Saturn in $\lambda = 0.85$ mm wavelength are shown in Fig. 1. The resultant synthesized beam of the image is $0.789″ \times 0.612″$.

3 Result

3.1 Rotational molecular emission line of HCN and CO in the atmosphere of Saturn

We detected the strong rotational emission line of HCN and CO at $\nu = 354.505$ and 345.795 GHz in the atmosphere of Saturn. The molecular rotational emission spectrums of HCN and CO in the atmosphere of Saturn are shown in Fig. 2 and 3. The molecular properties of detected HCN and CO species are shown in Tab. 1. The spectral peak of hydrogen cyanide and carbon monoxide emission lines were verified using the online Splatalogue database for astronomical molecular spectroscopy.

We calculate the column density of HCN and CO using the total column density ($N_{\text{tot}}$) equation in Mangum and Shirley (2015). The column density value is used to determine the abundance of molecular species. The total statistical column density of HCN is $N(\text{HCN}) \sim 2.42 \times 10^{16}$ cm$^{-2}$ and CO is $N(\text{CO}) \sim 5.82 \times 10^{17}$ cm$^{-2}$. We use the one-dimensional non-LTE radiative transfer code RADEX (van der Tak et al., 2007) to determine the excitation temperature of the detected HCN and CO molecule using the column density parameter. The excitation temperature of HCN is $T_{\text{ex}} = 18.48$ K and that of CO is $T_{\text{ex}} = 29.25$ K. The final resultant spectrum fit with XCLASS package using CASA with molfit file. The fractional abundance of HCN and CO in the atmosphere of Saturn with respect to H$_2$ is $f(\text{HCN}) \sim 1.02 \times 10^{-9}$ and $f(\text{CO}) \sim 2.42 \times 10^{-8}$. Our calculated mixing ratio of HCN and CO is similar with Lellouch et al. (1984) and Cavalié et al. (2010).

Now there is the big question that arises, our HCN emission line feature at 354.505 GHz is very similar to that observed in infrared (Lellouch et al., 1984) but previously CO molecular line at 345.795 GHz was shown the absorption feature (Cavalié et al., 2010) and we found the emission feature. Earlier, Cavalié et al. (2010) explained both emission and absorption features of CO(6–5) and CO(3–2) transition lines satisfied the comet impact model. The emission and absorption feature of CO(3–2) at 345.795 GHz both satisfied the same cometary model according to Cavalié et al. (2010) because the mixing ratio of CO emission line is $2.42 \times 10^{-8}$ (our paper) and the absorption line is $2.5 \times 10^{-8}$ Cavalié et al. (2010), which are very close.

3.1 http://ssd.jpl.nasa.gov/horizons.cgi
4 https://splatalogue.online/
5 https://xclass.astro.uni-koeln.de/Home
3.2 Predicted chemical pathways to the formation of HCN in the atmosphere of Saturn

The atmosphere of Saturn primarily consists of H₂, CO₂, CO, and CH₄ which are very essential for the production of HCN. The formation of HCN in the nitrogen-based atmospheres requires the N≡N bond and it needs to find a carbon atom. First, the nitrogen bond is split from NH₃, and second, carbon molecules need to win over oxygen for the competition of getting free nitrogen. The first condition is very easy because NH₃ molecules are present in the atmosphere of Saturn, which has a large absorption cross-section over N₂ (Lellouch et al., 1984). The hot temperature is necessary to split the hydrogen atom from NH₃.

After the split of the nitrogen bond, it reacts with nearby molecules as well as other stable molecules. The single nitrogen atom finds another single nitrogen atom to create N₂. We already know a big amount of H₂ exists in the atmosphere of Saturn. So the nitrogen is rapidly reacted with hydrogen to create NH₂ and then will continue to react with abundant hydrogen to the formation of NH₄. Similarly, the nitrogen atom reacts with the oxygen atom to produce NO₂. The trace species HCN are producing in the atmosphere of Saturn if the nitrogen bonds are reacted with carbon and hydrogen. In the atmosphere of Saturn, the carbon to oxygen balance is a key to understand nitrile chemistry. Fig. 4 provides the possible reaction of the chemical network to the formation of HCN from CO₂, CO, CH₄ in the atmosphere of Saturn via photochemical pathways.

The formation mechanism of HCN in the atmosphere of Saturn is varied with temperature, molecular composition, impact rate, surface process, and rate of lighting. In the atmosphere of Saturn, the HCN can be produced by the photochemical pathways and atmospheric lightning. In our predicted chemical reaction, some reactions are photochemical which denoted as hν and it requires photon for the production of HCN. We used the STAND2019 chemical network for chemical modeling which is a modification of the STAND2016 network (Rimmer & Helling, 2016) which includes H/C/N/O chemistry with 3 carbons, 2 nitrogens, 3 oxygens, and 8 hydrogens and valid up to 30000 K temperature and also include some gas-phase reactions involving Na, K, Mg, Fe, Ti, Si, and Cl. The STAND2019 chemical network included 5000 reactions involving over 350 amount of chemical species. In the planetary atmosphere, CO₂ and CH₄ are very important species for the formation of other molecular gas due to photochemical reaction.

4 Discussion

In this letter, we present the spectroscopic detection of the rotational molecular emission line of hydrogen cyanide (HCN) at frequency $\nu = 354.505$ GHz and carbon monoxide at $\nu = 345.795$ GHz with $\geq 4\sigma$ significance using ALMA band 7 observation. The fractional abundance of HCN and CO is $f($HCN$) \sim 1.02 \times 10^{-9}$ and $f($CO$) \sim 2.42 \times 10^{-8}$. Our calculated mixing ratio of HCN and CO in the atmosphere of Saturn is very similar to Lellouch et al. (1984) and Cavalié et al. (2010). In the atmosphere of Saturn, HCN is produced due to the photochemical reaction of CO₂ and CH₄.
The discovery of HCN in the atmosphere of Saturn fills a crucial gap in our knowledge of the solar system’s molecular chemistry. Earlier, Hydrogen cyanide (HCN) was found in the atmosphere of Saturn moon Titan (Molter et al., 2016). The discovery of an HCN emission line in the atmosphere of Saturn may be crucial in the formation of certain complex bio substances, as well as prebiotic molecules. Without the existence of HCN, CO, and H₂O (Hesman, 2015), the development and evolution of prebiotic molecules with carbon-based metabolism is difficult in the atmosphere of Saturn. In the Strecker synthesis reaction, the HCN gas is reacted with NH₃ and aldehyde to form different types of amino acids (Strecker, 1854). According to Miller and Urey’s experiment (Miller, 1953), the existence of HCN, CO, H₂O, and other carbon-based molecules gives assurance in the probability of amino acid formation in the atmosphere of Saturn. The nucleobase C₂H₅N₅ is made up of five HCN bound molecules. The HCN was recently discovered to be present in photochemical reactions that create lipids, amino acids, and nucleosides, the three basic building blocks of life (Ritson & Sutherland, 2012; Patel et al., 2015; Xu et al., 2018). The UV light is absorbed by HCN and H₂S, or bisulfite in H₂O. The UV photon causes an electron to be photo detached from H₂S or bisulfite, and the solvated electron reduces HCN to form an imine complex, which then hydrolyzes to form formaldehyde. The dissociated cyanide products interacting with the product sugars will continue this photochemical homologation. Other possible HCN-derived feedstock molecules, such as cyanamide and cyanoacetylene, react with the sugars to form pyrimidine nucleotides. Furthermore, these feedstock compounds, along with methylamine and nitrogen oxides, serve as activators to facilitate the ligation of these building blocks into polypeptides, a crucial next step in prebiotic chemistry (Mariani et al., 2018). In the atmosphere of Saturn, further spectroscopic observations of the complex molecular gas will aid in confirming the origin and formation mechanism of the observed trace gases.

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