

# Detection of simplest amino acid *glycine* in the atmosphere of the Venus

Arijit Manna,<sup>1</sup> Sabyasachi Pal,<sup>2,1\*</sup> Mangal Hazra<sup>1</sup>

<sup>1</sup>Midnapore City College, Kuturia, Bhadutala, Paschim Medinipur, West Bengal, India 721129

<sup>2</sup>Indian Centre for Space Physics, 43 Chalantika, Garia Station Road, Kolkata, India 700084

\* E-mail: sabya.pal@gmail.com

Amino acids are considered to be prime ingredients in chemistry, leading to life. Glycine is the simplest amino acid and most commonly found in animal proteins. It is a glucogenic and non-essential amino acid that is produced naturally by the living body and plays a key role in the creation of several other important bio-compounds and proteins. We report the spectroscopic detection of the presence of the simplest amino acid glycine ( $\text{NH}_2\text{CH}_2\text{COOH}$ ) with transition  $J=13(13,1)-12(12,0)$  at  $\nu=261.87$  GHz ( $16.7\sigma$  statistical significance) with column density  $N(\text{glycine})=7.8\times 10^{12}$   $\text{cm}^{-2}$ , in the atmosphere of the solar planet Venus using the Atacama Large Millimeter/submillimeter Array (ALMA). Its detection in the atmosphere of Venus might be one of the keys to understand the formation mechanisms of prebiotic molecules in the atmosphere of Venus. The upper atmosphere of Venus may be going through nearly the same biological method as Earth billions of years ago.

## INTRODUCTION

Averaged surface temperature of Venus is highest among solar system bodies ( $\sim 740$  K) (1) but in the middle and upper atmosphere, the temperature drops making a relatively hospitable environment for life. The temperature of clouds at the height of 50 km is 300–350 K with pressure around 1 bar, which is comparable to Earth ground temperature and pressure (2). So, Venus has been regarded as a possible sustainer of life for a long time (3, 4). The atmosphere of Venus is extremely dense and mostly consists of CO<sub>2</sub> (96.5%), N<sub>2</sub> (3.5%) and trace gases (5). The mesosphere of Venus (60–120 km altitude) poses complex cycles of dynamic processes and photochemistry that are still poorly understood. Earlier, it is shown in the laboratory that organic molecules, including glycine, can be produced in a Venus like atmosphere with a gas mixture of N<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>O, O<sub>2</sub> and CO<sub>2</sub> in presence of a 60 kV spark (6). Recently PH<sub>3</sub> was detected from Venusian atmosphere (7) which can not be explained by conventional processes known to us and may be due to unknown geo-chemistry, photo-chemistry, or even aerial microbial life present in upper Venus atmosphere as Earth phosphine is mostly related with biological sources (8).

Glycine is the simplest amino acid and is regarded as the basic building block leading to life. In Earth, it is most commonly found in animal proteins. Glycine is a non-essential amino acid and is naturally formed by the living body on Earth and plays an important role in the development of many other important bio-compounds and proteins. Detection of bio-molecules, specially amino acids, outside Earth gives important clue in the understanding of formation and evolution of life outside our planet. It is generally believed that formation of glycine may have occurred in the interstellar medium (ISM) as amino acids, including glycine is detected in meteorites (9). But, after a tentative detection of glycine in interstellar medium (10), a rigorous study verifies that there is no proof of the presence of glycine in interstellar medium (11).

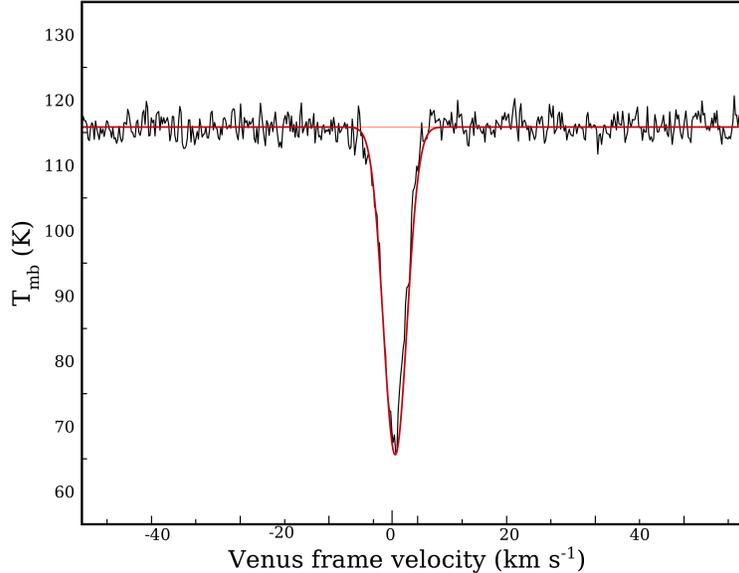


Figure 1: Absorption spectrum of the  $\text{NH}_2\text{CH}_2\text{COOH}$  ( $J=13(13,1)-12(12,0)$ ) with single gaussian fitting ( $\text{FWHM}=1.38\pm 0.07 \text{ km s}^{-1}$ ). The spectrum was made by integrating the reduced ALMA data cubes from the centre of Venus (12579.1 km at Venus’ distance) within a circular region of  $25.2''$  diameter. The continuum emission from Venus is subtracted from the spectrum.

## RESULTS AND DISCUSSION

We used interferometric millimetre observation of Venus using the Atacama Large Millimeter/submillimeter Array (ALMA) (for details, see ‘ALMA data reduction’ in Methods). During the observation, the distance between Earth and Venus was 0.691 AU and the angular diameter of Venus was  $24.15''$ . The illumination factor was 51.4% which means about half of the mapped planet was in day side. Fig. 1 shows the absorption spectrum of glycine. The spectrum was made by integrating the reduced ALMA data cubes from the centre of Venus (12579.1 km at Venus’ distance) within a circular region of  $25.2''$  diameter. Spectral peaks were allocated to frequencies obtained from the JPL catalogue and the Cologne Database for Molecular Spectroscopy (12). Using the Venus ephemeris, frequency channels were mapped to velocity channels so that in the final image cubes,  $0 \text{ km s}^{-1}$  corresponds to line frequency in the

Table 1: Properties of  $\text{NH}_2\text{CH}_2\text{COOH}$  absorption line for different regions of Venus atmosphere

Latitude range	FWHM ( $\text{km s}^{-1}$ )	Signal to noise ratio
$0^\circ\text{--}22.5^\circ$	$1.12\pm 0.02$	14.2
$22.5^\circ\text{--}45.0^\circ$	$1.38\pm 0.07$	16.6
$45.0^\circ\text{--}67.5^\circ$	$1.12\pm 0.07$	16.6
$68.5^\circ\text{--}90.0^\circ$	–	$< 3\sigma$

planetary-motion frame of Venus. The spectrum is fitted with single Gaussian at 361.8739 GHz with transition  $J=13(13,1)\text{--}12(12,0)$  with an area of absorption spectra= $0.0640\pm 0.0004$  K  $\text{km s}^{-1}$  (FWHM= $1.38\pm 0.07$   $\text{km s}^{-1}$ ). Glycine absorption line is easily detected with  $16.7\sigma$  statistical significance. A width of a few  $\text{km s}^{-1}$  in glycine spectra is typical of absorptions from the upper atmosphere of Venus (13). Earlier, glycine was detected in comet 81P/Wild 2 (14) and 67P/Churyumov-Gerasimenko (15) but this is the first time the presence of an amino acid is reported on a planet or moon.

Glycine is detected strongly near the equator of Venus and mid-latitude as summarised in Table 1. The grid based spectrum from different part of Venus is shown as Fig. 4 of supplementary materials. Distribution of glycine is stronger in mid latitude ( $22.5^\circ\text{--}67.5^\circ$ ) compared to the equator. Near the pole, there is no evidence of the presence of glycine ( $< 3\sigma$ ). Recently, the presence of  $\text{PH}_3$  in Venus was also found to be stronger near mid latitude and it was not detected by ALMA beyond  $60^\circ$  latitude (7). The mid-latitude Hadley circulation may give the most stable life supporting condition with circulation times of 70–90 days being sufficient for (Earth-like) microbial life reproduction (4, 7). At height 65–70 km, zonal wind blow at a nearly constant velocity  $\sim 100$   $\text{m s}^{-1}$  between latitude range  $50^\circ\text{N}$  to  $50^\circ\text{S}$  and then air speed gradually decrease towards pole (16). The latitude dependent distribution of glycine roughly matches (within  $\sim 10^\circ$ ) with the detection limit of recently detected phosphine (7) and with the proposed upper Hadley-cell boundary (16) where gas circulates between upper and lower altitudes.

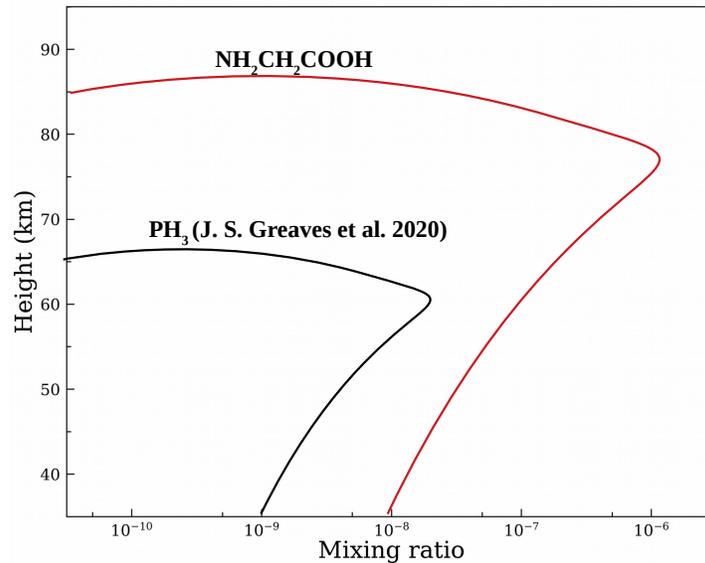


Figure 2: Mixing ratio of  $\text{NH}_2\text{CH}_2\text{COOH}$  as a function of atmosphere height (km) within cloud layer ( $\sim 75\text{-}80$  km) (red curve), compared with the  $\text{PH}_3$  (7) (black curve).

During our observation of Venus, the illumination factor was 51.2% indicating near half of the measurements was taken from the day side of Venus and the other half from the night side. No measurable difference between regions with day and night time was found for the detection of glycine.

We also detected ethyl cyanide ( $\text{CH}_3\text{CH}_2\text{CN}$ ) at  $\nu=259.869$  GHz with transition  $J=29(12,17)\text{-}28(12,16)$  in the atmosphere of Venus (as shown in Fig. 3 of supplementary materials). The line is comfortably detected with  $9.8\sigma$  statistical significance. The  $\text{CH}_3\text{CH}_2\text{CN}$  absorption line was fitted with a single Gaussian function with an area of absorption spectra= $0.0051 \pm 0.0002$  K  $\text{km s}^{-1}$ . The column density of ethyl cyanide is  $5.21 \times 10^{14} \text{ cm}^{-2}$ . Earlier, ethyl cyanide was detected in the atmosphere of Saturn's largest moon Titan (17). Titan is the only moon in the solar system which is known to harbour dense atmosphere (18). Like Venus, Titan also has methane (19) and ethane (20) clouds in its atmosphere.

The radiative transfer in the atmosphere of Venus was calculated assuming a spherically-

homogeneous, multilayered model, with mixing ratio and altitude from the Venus International Reference Atmosphere (VIRA) (21). The one-dimensional photochemistry-diffusion code ARGO (22) is used to solve the atmospheric transport equation for the steady-state vertical composition profile. We used STAND2015 (22) for the chemical network, which includes H/C/N/O species. A limited S/Cl/P network relevant for the atmosphere of Venus is also added by using the middle atmosphere network of Zhang (23) and the low atmospheric network of Krasnopolsky (24). The atmosphere from the Venusian surface to 140 km is divided into many layers of 1 km depth and temperature profile from VIRA is used which is established from spacecraft temperature measurements.

Miller and Urey's experiment in 1953 (25) simulated the primordial Earth conditions and tested the chemical origin of life in the Earth atmosphere. The experiment used water (H<sub>2</sub>O), methane (CH<sub>4</sub>), ammonia (NH<sub>3</sub>), and hydrogen (H<sub>2</sub>) and produced many organic compounds including glycine and different types of other amino acids. A recent experiment with the preserved laboratory materials of Miller synthesized more than 40 different amino acids and amines which shows possibilities of formation of biological compounds under different cosmogeochemical conditions (26). Miller and Urey's experiment found glycolic acid (CH<sub>2</sub>OHCOOH) which produces the simple amino acid glycine when it reacts with ammonia (NH<sub>3</sub>) (CH<sub>2</sub>OHCOOH + NH<sub>3</sub> → CH<sub>2</sub>NH<sub>2</sub>COOH + H<sub>2</sub>O). Since HDO (27), CH<sub>4</sub> (27), NH<sub>3</sub> (28), and CO<sub>2</sub> (29) is already detected in the Venus atmosphere, it is possible that glycine formed following route of Miller and Urey experiment. Alternatively, glycine may have been also formed by a reaction between NH<sub>3</sub>, CH<sub>2</sub> and CO<sub>2</sub> all of which are already present in Venus atmosphere (NH<sub>3</sub>+CH<sub>2</sub>+CO<sub>2</sub> → CH<sub>2</sub>NH<sub>2</sub>COOH) (30). Recently, amino acid decomposition has been reported in high-pressure and high-temperature water (31). These decomposition reactions in condensed systems seem to be irreversible but in the gas phase, there may be reverse reaction routes producing amino acids.

In astrophysics, chemical physics and biophysics, synthetic reaction routes of the simplest amino acid glycine, from simple molecules have great significance with chemical evolution and the origin of life (32). The detection of glycine in the atmosphere of Venus may indicate the existence of an early form of life in the atmosphere of the solar planet because amino acid is a building block of protein (33). Venus may be going through the primary stage of biological evolution. It should be noted that detection of glycine in Venus atmosphere is a hint of the existence of life but not a robust evidence. Though in Earth, glycine produces by biological procedures, it is possible that in Venus glycine is produced by other photochemical or geochemical means, not common on Earth. Other glycine spectral signature and detailed simulation of the various pathways to glycine in Venusian atmospheric condition should be studied in future. A Venus mission with direct sampling from Venusian surface and cloud may confirm the source of glycine in the planet.

## References

1. M. Y. Marov et al., Preliminary results on the Venus atmosphere from the Venera 8 descent module. *Icarus* **20**, 407–421 (1973).
2. C. S. Cockell, Life on Venus. *Planetary and Space Science* **47**, 1487–1501 (1999).
3. C. Sagan, Life on the Surface of Venus? *Nature* **216**, 1198–1199 (1967).
4. D. H. Grinspoon, M. A. Bullock, in *Exploring Venus as a Terrestrial Planet* (eds L. W. Esposito, E. R. Stofan, T. E. Cravens) (American Geophysical Union, 2007), pp. 191.
5. J. Bertaux et al., A warm layer in Venus' cryosphere and high-altitude measurements of HF, HCl, H<sub>2</sub>O and HDO. *Nature* **450**, 646–649 (2007).

6. V. A. Otroshchenko, Yu. A. Surkov, The possibility of organic molecule formation in the Venus atmosphere. *Origins Life Evol Biosphere* **5**, 487–490 (1974).
7. J. S. Greaves et al., Phosphine gas in the cloud decks of Venus. *Nature Astronomy* (2020).
8. W. Bains et al., Phosphine on Venus Cannot be Explained by Conventional Processes. arXiv:2009.06499 (2020).
9. S. Pizzarello, R. V. Krishnamurthy, S. Epstein, J. R. Cronin, Isotopic analyses of amino acids from the Murchison meteorite. *GeCoA* **55**, 905–910 (1991).
10. Y. J. Kuan, S. B. Charnley, H. C. Huang, W. L. Tseng, Z. Kisiel, Interstellar glycine. *Astrophys.J.* **593**, 848–867 (2003).
11. L. E. Snyder et al., A rigorous attempt to verify interstellar glycine. *Astrophys.J.* **619**, 914–930 (2005).
12. H. S. P. Müller, S. Thorwirth, D. A. Roth, G. Winnewisser, The Cologne Database for Molecular Spectroscopy, CDMS. *A&A* **370** L49–L52 (2001).
13. T. Encrenaz, R. Moreno, A. Moullet, E. Lellouch, T. Fouchet, Submillimeter mapping of mesospheric minor species on Venus with ALMA. *Planet. Space Sci.* **113**, 275–291 (2015).
14. J. E. Elsila, D. P. Glavin, J. P. Dworkin, Cometary glycine detected in samples returned by Stardust. *Meteoritics & Planetary Science* **44**, 1323–1330 (2009).
15. K. Altwegg et al., Prebiotic chemicals-amino acid and phosphorus-in the coma of comet 67P/Churyumov-Gerasimenko. *Science Advances* **2**, (2016).
16. A. Sánchez-Lavega, S. Lebonnois, T. Imamura, P. Read, D. Luz, The atmospheric dynamics of Venus. *Space Sci. Rev.* **212**, 1541–1616 (2017).

17. M. Cordiner et al., Ethyl Cyanide On Titan: Spectroscopic Detection and Mapping Using Alma. *Astrophysical Journal* **800**, 14–20 (2014).
18. R.M.C. Lopes et al., Titan as Revealed by the Cassini Radar. *Space Sci Rev* **215**, 33–82 (2019).
19. R. Hueso, A. Sánchez-Lavega, Methane storms on Saturn’s moon Titan. *Nature* **442**, 428–431 (2006).
20. C. A. Griffith et al., Evidence for a Polar Ethane Cloud on Titan. *Science* **313**, 1620–1622 (2006).
21. V. I. Moroz, G. M. Keating, A. Kliore, The Venus International Reference Atmosphere (United Kingdom: Committee on Space Research, 1986), v. 5, pp. 303.
22. P. B. Rimmer, C. Helling, A Chemical Kinetics Network for Lightning and Life in Planetary Atmospheres. *The Astrophysical Journal Supplement Series* **224**, 9 (2016).
23. X. Zhang, M. C. Liang, F. P. Mills, D. A. Belyaev, Y. L. Yung, Sulfur chemistry in the middle atmosphere of Venus. *Icarus* **217**, 714–739 (2012).
24. V. A. Krasnopolsky, Chemical kinetic model for the lower atmosphere of Venus. *Icarus* **191**, 25–37 (2007).
25. S. L. Miller, Production of Amino Acids Under Possible Primitive Earth Conditions. *Science* **117**, 528 (1953).
26. J. L. Bada, New insights into prebiotic chemistry from Stanley Miller’s spark discharge experiments. *Chem. Soc. Rev.* **42**, 2186–2196 (2013).

27. T. Donahue, R. R. Hodges, Venus methane and water. *Geophysical Research Letters* **20**, GL00513 (1993).
28. K. Goettel, J. Lewis, Ammonia in the Atmosphere of Venus. *Journal of The Atmospheric Sciences*, 828–830 (1974).
29. M. Snels, S. Stefani, D. Grassi, G. Piccioni, A. Adriani, Carbon dioxide opacity of the Venus' atmosphere. *Planetary and Space Science* **103**, 347–354 (2014).
30. S. Maeda, K. Ohno, No activation barrier synthetic route of glycine from simple molecules (NH<sub>3</sub>, CH<sub>2</sub>, and CO<sub>2</sub>) via carboxylation of ammonium ylide: A theoretical study by the scaled hypersphere search method. *Chemical Physics Letters* **398**, 240–244 (2004).
31. N. Sato, A. T. Quitain, K. Kang, H. Daimon, K. Fujie, Reaction Kinetics of Amino Acid Decomposition in High-Temperature and High-Pressure Water. *Ind. Eng. Chem.* **43**, 3217–3222 (2004).
32. A. Gutiérrez-Preciado, H. Romero, M. Peimbert, An Evolutionary Perspective on Amino Acids. *Nature Education* **3**, 29 (2010).
33. K. Norio, M. Shigenori, Origins of building blocks of life: A review. *Geoscience Frontiers* **9** (2017).

## **Acknowledgements**

This paper makes use of the following ALMA data: ADS/JAO.ALMA#2018.1.00879.S. ALMA is a partnership of ESO (representing its member states), NSF (USA) and NINS (Japan), together with NRC (Canada), MOST and ASIAA (Taiwan), and KASI (Republic of Korea), in cooperation with the Republic of Chile. The Joint ALMA Observatory is operated by ESO,

AUI/NRAO and NAOJ. The authors declare no competing interests. All data presented in the manuscript or the supplementary materials are available.

## List of Supplementary Materials

### Method

Fig 3: The spectral map of  $\text{NH}_2\text{CH}_2\text{COOH}$  ( $J=13(13,1)-12(12,0)$  at  $\nu=261.87$  GHz) and  $\text{CH}_3\text{CH}_2\text{CN}$  ( $J=29(12,17)-28(12,16)$ ) at  $\nu=259.869$  GHz spectra from ALMA showing variation of absorption features in different part of the planet. Both glycine and ethyle cyanide are easily detected in most of the individual grid below latitude  $67.5^\circ$ . The angular diameter of the planet on the day of observation was  $24.15''$ . The planet is shown by a red circle.

Fig 4: The spectral map of  $\text{NH}_2\text{CH}_2\text{COOH}$  ( $J=13(13,1)-12(12,0)$  at  $\nu=261.87$  GHz) and  $\text{CH}_3\text{CH}_2\text{CN}$  ( $J=29(12,17)-28(12,16)$ ) at  $\nu=259.869$  GHz from ALMA showing variation of absorption features in different part of the planet. Both glycine and ethyle cyanide are easily detected in most of the individual grids below latitude  $67.5^\circ$ . The angular diameter of the planet on the day of observation was  $24.15''$ . The planet is shown by a red circle.

References (34)

## Supplementary Materials

### METHOD

#### ALMA data reduction

We used high resolution interferometric millimetre-wave data using the Atacama Large Millimeter/submillimeter Array (ALMA) to study Venus. The 41 minute observation took place on 8th January 2019 beginning 11h:05m:22.6s UTC. During the observation, the angular diameter of Venus was  $24.15''$  with illumination factor of 51.2% and surface brightness  $1.4 \text{ mag arcsec}^{-2}$ . The correlator was configured so that eleven spectral windows was used inside ALMA Band 6

with frequency range 245.19–282.23 GHz with 1024 channels. The channel spacing was 244 kHz, leading to a spectral resolution of 488 kHz (or  $3.6 \text{ km s}^{-1}$ ) following Hanning’s smoothing by the correlator. The XX and YY type signal substances were tested via an integration time of 390.97 seconds. A total of 11 antennas were accessible during observation. The telescope was configured to track the NASA Horizon ephemeris position of Venus with real-time updating of the coordinates of the phase centre. The source J1256–0547 was used as a bandpass and flux calibrator while J1512–0905 was used as an amplitude and phase calibrator. Calibration and flagging of bad data were done by using software package Common Astronomy Software Application (CASA 5.1.1–5). The measured continuum flux density was set using the Butler-JPL-Horizons 2012 standard (32) and the NASA ephemeris. The emission from line-free channels in the calibrated visibility spectral tables was averaged to produce continuum visibilities for an image of the continuum emission from Venus. The continuum emission was subtracted from the visibility spectra by fitting the line-free channels with a polynomial function of the first order. The imaging was performed using the `clean` task in CASA. Hogbom algorithm was used to perform deconvolution of the point-spread function (PSF) for each spectral channel, with a threshold flux level of twice the expected RMS noise and natural visibility weighting. The resulting spatial resolution (FWHM of the Gaussian restoring beam) was  $24''.1 \times 22''.3$  (with position angle 80 degree). At Venus geocentric distance of 0.691 AU at the time of observation, this resolution corresponds to  $12077.98 \text{ km} \times 11175.89 \text{ km}$  (compared with Venus’ 12,104 km diameter).

## References

34. B. Butler, ALMA Memo 594: Flux Density Models for Solar System Bodies in CASA, ALMA Memo Series, NRAO (2012).

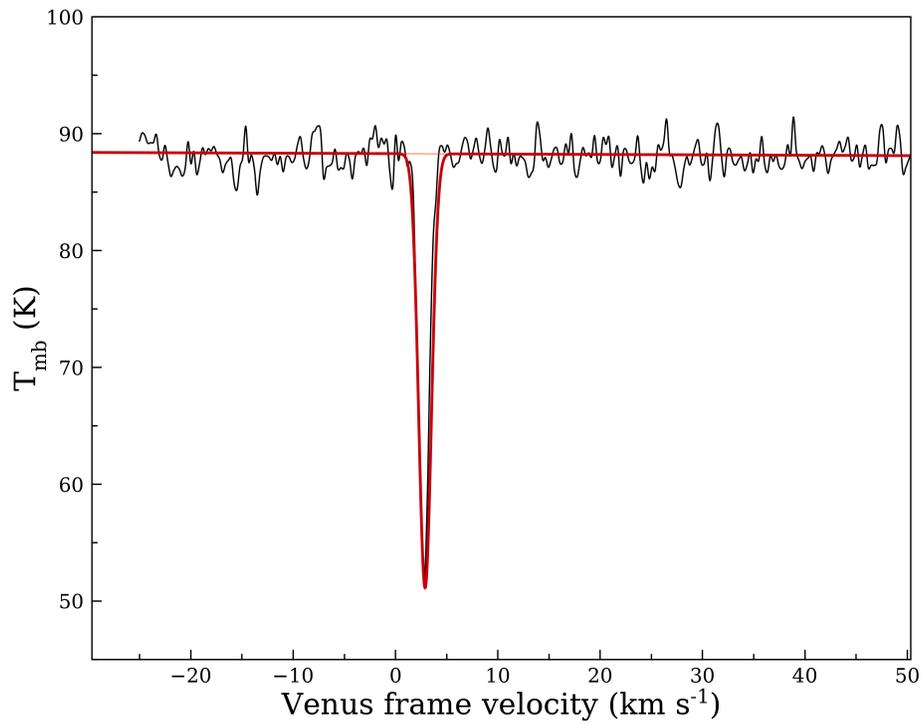


Figure 3: Absorption spectrum of CH<sub>3</sub>CH<sub>2</sub>CN (J=29(12,17)–28(12,16)) at  $\nu=259.869$  GHz with single gaussian fitting (FWHM= $0.73\pm 0.02$  km s<sup>-1</sup>). The spectrum was made by integrating the reduced ALMA data cubes from the centre of Venus (12579.1 km at Venus' distance) within a circular region of 25.2'' diameter. The continuum emission of Venus is subtracted from the spectrum.

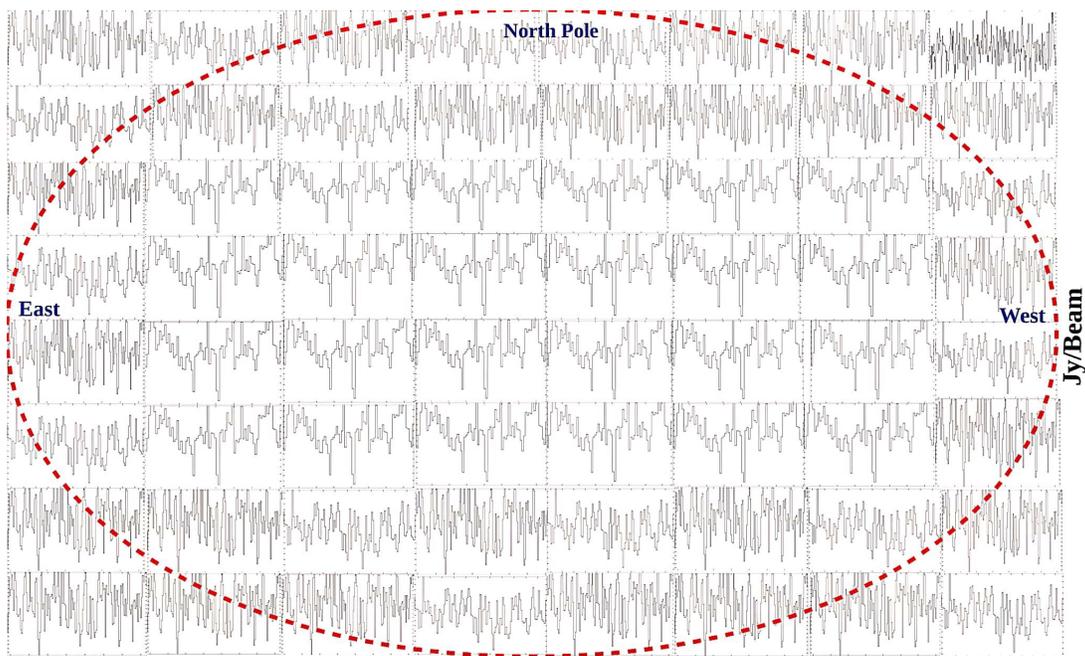


Figure 4: The spectral map of  $\text{NH}_2\text{CH}_2\text{COOH}$  ( $J=13(13,1)-12(12,0)$  at  $\nu=261.87$  GHz) and  $\text{CH}_3\text{CH}_2\text{CN}$  ( $J=29(12,17)-28(12,16)$ ) at  $\nu=259.869$  GHz from ALMA showing variation of absorption features in different part of the planet. Both glycine and ethyle cyanide are easily detected in most of the individual grids below latitude  $67.5^\circ$ . The angular diameter of the planet on the day of observation was  $24.15''$ . The planet is shown by a red circle.