Observation of DCl and upper limit to NH₃ on Venus

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A B S T R A C T

To search for DCl in the Venus atmosphere, a spectrum near the D35Cl (1–0) R4 line at 2141.54 cm⁻¹ was observed using the CHESL spectrograph at NASA IRTF. Least square fitting to the spectrum by a synthetic spectrum results in a DCl mixing ratio of 17.8 ± 6.8 ppb. Comparing to the HCl abundance of 400 ± 30 ppb (Krasnopolsky [2010a] Icarus, 208, 314–322), the DCl/HCl ratio is equal to 280 ± 110 times the terrestrial DCl/HCl ratio is equal to 280 ± 110 times the terrestrial DCl/HCl ratio is equal to 280 ± 110 times the terrestrial

1. Observations

Here we will consider our search for two hydrogen-bearing species in the atmosphere of Venus. This search has been made by means of the ground-based high-resolution spectroscopy in the near infrared range. We used the long-slit spectrograph CSHELL at the NASA Infrared Telescope Facility (IRTF). The spectrograph selects a narrow spectral interval of 0.0023Δν₀, where ν₀ is the central wavenumber that may be chosen in the range of 1.08–5.6 μm. The instrument detector is an InSb array of 256 × 150 pixels cooled to 30 K. Each pixel is 9 × 10⁻⁶Δν₀ in the dispersion direction and 0.21 arcsec in the aspect direction. The instrument resolving power is ν/Δν = 40,000. The telescope diameter is 3 m, and its position on Mauna Kea (Hawaii) with elevation of 4.2 km, mean overhead water of 2 pr. mm, and pressure of 0.6 bar is favorable for high-resolution spectroscopy of the planetary atmospheres. Total spatial resolution of the telescope and the spectrograph is ~1 arcsec.

The observations were made on January 5, 2011, when the Venus diameter was 25.6 arcsec and covered almost full slit of 30 arcsec. Venus was near its maximum elongation with a phase (Sun-target-observer) angle of 92°, that is, the terminator was near the disk center with almost equal day and night sides. We placed the instrument slit in the middle of the dayside segment and parallel to the central meridian. The slit covered a latitude range of ±60° with local time of 08:00 at the low latitudes. Geocentric velocity of Venus was near its maximum value of 13 km s⁻¹ and resulted in a maximal Doppler shift to the red.

The observations involved exposures of Venus, the sky foreground 1 arc min off Venus, flat field from a continuum source, and dark current. The difference of the Venus and foreground spectra is divided by the difference of the flat field and dark current spectra. This frame of 150 spectra with 256 pixels in each spectrum is corrected to remove bad and icky pixels using mean values of their neighbors. Then each spectrum is transformed to 2048
sampling points using a parabolic interpolation that keeps a sum of eight sampling points equal to the pixel value (Krasnopolsky, 2007a). Next, a wavenumber scale is determined for each spectrum using identified absorption lines in the spectrum. Then the spectra are linearly interpolated to a uniform wavenumber scale with a step of 0.001 cm\(^{-1}\). These spectra may be used to search for a species and to study its spatial distribution. However, we sum up all the DCI and NH\(_3\) spectra to get mean abundances of these species on Venus.

2. Search for DCI at the Venus cloud tops

2.1. Motivation of the study

Deuterium on Venus has been detected as HDO and HD. A large D/H ratio in water on Venus was discovered by the mass spectrometer at the Pioneer Venus large probe (Donahue et al., 1982). The measured HDO/H\(_2\)O was equal to 100 ± 15 times the terrestrial value of HDO/H\(_2\)O = 3.11 × 10\(^{-6}\) (D/H = 1.56 × 10\(^{-4}\) is half this value). The observation was made in the cloud layer at 54 km. That was a clear indication of an enormous loss of hydrogen in the past with a strong isotope fractionation, that is, Venus was wet in the past. Later de Bergh et al. (1991) found HDO lines in high-resolution spectra of the nighttime thermal emission from the lower atmosphere at 2.3 \(\mu\)m; the retrieved D/H in H\(_2\)O was 120 ± 40 at 26–45 km. High-resolution spectroscopy from the Kuiper Airborne Observatory at the altitude of 12 km in the Earth’s atmosphere, that is, with very low overhead telluric water, resulted in D/H = 157 ± 15 at 72 km on Venus (Bjoraker et al., 1992). Finally, the SOIR occultations by the Venus Express orbiter give D/H = 240 ± 25 in water vapor at 70–95 km (Fedorova et al., 2008). Encrenaz et al. (1995) detected both H\(_2\)O and HDO lines in the millimeter range, and Sandor and Clancy (2005) observed the HDO millimeter lines to study variations of water vapor in the Venus mesosphere.

Recently Matsui et al. (2012) observed the HDO abundance of 0.22 ± 0.03 ppb using the HDO lines at 2.3 \(\mu\)m. They assign the observed values to 62 km. Observations by Krasnopolsky (2010a) at 2.3 \(\mu\)m gave a reference altitude of 68 km in this spectral region. The difference may appear because Matsui et al. (2012) referred the observed HDO to the bottom of the CO\(_2\) layer at 2.3 \(\mu\)m while Krasnopolsky (2010a) considered the middle of the CO\(_2\) layer with pressure smaller by a factor of 2. The H\(_2\)O abundance has not been observed by Matsui et al. (2012), and their D/H that was based on the adopted 5 ppm of H\(_2\)O is actually very uncertain because of the significant variations of H\(_2\)O. Measurements of the HDO/H\(_2\)O ratio require simultaneous observations of both species. For example, Encrenaz et al. (1995), Sandor and Clancy (2005), and Krasnopolsky (2010b) observed HDO but did not attempt to get the HDO/H\(_2\)O ratio without simultaneous observations of H\(_2\)O.

The measured D/H ratios show a gradual increase from the lower atmosphere to mesosphere by a factor of 2, and the observed increase exceeds the claimed uncertainties. However, a photochemical model for H\(_2\)O, HCl, HDO, and DCI at 58–112 km (Liang and Yung, 2009) resulted in a constant D/H ratio with a minor increase by 10% above 100 km. Differences in photolysis cross sections of H\(_2\)O and HDO (Cheng et al., 1999) and HCl and DCI (Bahou et al., 2001) were the only fractionation factors in the model. According to Bahou et al. (2001), photolysis of HCl is more efficient than that of DCI by a factor of 6.

The ion mass spectrometer at the Pioneer Venus orbiter observed a mass 2 peak that was initially assigned to H\(_2\). However, McElroy et al. (1982) proposed that this peak reflects atomic deuterium. Analysis by Hartle and Taylor (1983) confirmed this identification and resulted in D/H = 140 ± 40 times the terrestrial ratio in H\(_2\) in the upper atmosphere near 150 km.

Overall, while the huge enrichment in the deuterium abundance is obvious in the Venus atmosphere, a nature of the observed variations of D/H remains unclear. That was the motivation of our search for DCI.

2.2. Observed spectrum of DCI

The spectroscopic database HITRAN-2008 (Rothman et al., 2009) does not include DCI, and we searched for the DCI line wavenumbers and strengths in the literature. The HCl mixing ratio is 400 ppb at 74 km on Venus (Krasnopolsky, 2010a), and the expected DCI abundance is very small, 12.5 ppb for D/H ≈ 200. Therefore, we should use the strongest DCI lines for its detection. That is why we choose D\(^{35}\)Cl, which is more abundant than D\(^{37}\)Cl by a factor of 3, and the fundamental (1–0) band at 2091 cm\(^{-1}\), which is stronger than the overtone (2–0) at 4129 cm\(^{-1}\) by a factor of 60 (Benedit et al., 1957). All lines of the (1–0) band are strongly contaminated by other lines in the atmospheres of the Earth and Venus; the contamination by CO\(_2\) and CO lines originates from Venus and cannot be removed by a proper Doppler shift. Our analysis showed that the DCI R4 line at 2141.540 cm\(^{-1}\) is the best for the observation, though it is contaminated by CO\(_2\), CO, and H\(_2\)O lines. Wavenumbers of the DCI lines are taken from Kleey and Ogilvie (1993). The R4 line is the strongest, and its strength is 1.32 × 10\(^{-19}\) cm at 300 K (Benedict et al., 1957). Calculations for 220–250 K give (1.51–1.45) × 10\(^{-19}\) cm, and we will adopt S = 1.47 × 10\(^{-19}\) cm.

The observed and processed spectrum is shown in Fig. 1. It includes two CO hot emission lines that are excited by photolysis of CO\(_2\) and by absorption of the sunlight by the CO (2–0) band at 2.35 \(\mu\)m (Crovisier et al., 2006). The other features are the absorption lines of CO\(_2\) and CO from Venus, telluric lines of H\(_2\)O, and the solar lines. Weak telluric lines of CO\(_2\), N\(_2\)O, and O\(_3\) are present as well. The expected Doppler-shifted position of the DCI line is on the red wing of a blend at 2141.48 cm\(^{-1}\). This blend is formed by the Venus CO\(_2\) and CO lines and the telluric H\(_2\)O line.

We choose an interval of 2140.7–2142.0 cm\(^{-1}\) for fitting by a synthetic spectrum (Fig. 2). It contains strong CO\(_2\), CO, and solar lines that may constrain the lines in the blend. Fitting parameters for the synthetic spectrum are the CO\(_2\), CO, and DCI abundances.
with and without DCl are shown green in Fig. 2. These difference (Hase et al., 2010). The telluric H2O mean temperature and pres-
clouds, H2O abundance and fixed CO2, N2O, and O3 abundances
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wavenumber corrections, and four parameters for the continuum
variation. A solar to thermal emission ratio in the spectrum of
Venus is another Venus parameter. The solar spectrum is taken
from the ACE orbiter observations with resolution of 0.02 cm\(^{-1}\)
(Hase et al., 2010). The telluric H2O mean temperature and pres-
sure are fixed at 270 K and 0.5 bar, those for CO2 and N2O are
230 K and 0.3 bar (half total pressure and temperature at this
level), and 230 K and 25 mbar for O3.

The least square fit synthetic spectrum is shown in Fig. 2. Differ-
esences between the observed spectrum and the synthetic spectra
with and without DCI are shown green in Fig. 2. These difference
spectra smoothed within 0.07 cm\(^{-1}\) are depicted as the black
curves. This interval accounts for 90% of the total absorption effect
for a line at the instrument spectral resolution. The DCI absorption
in the synthetic spectrum and that smoothed within 0.07 cm\(^{-1}\)
are shown red. An uncertainty of the observation and fitting is equal to
standard deviation of the black solid curve corrected by a factor of
1.10. Here 68 is the number of degrees of

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A part of the spectrum from Fig. 1 (red) that is fitted by a synthetic spectrum (blue). Their differences with (solid) and without (dashed) DCI line are shown green in Fig. 2. These differences smoothed within 0.07 cm\(^{-1}\) are black, and the unsmoothed and smoothed contributions of the DCI line are red. The error bars reflect standard deviation of the black curve corrected for the number of fitting parameters. The retrieved DCI line is scaled to the CO2 lines to get a DCI mixing ratio of 17.8 ± 6.8 ppb. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The HCl mixing ratio is 400 ± 30 ppb at 74 km (Krasnopolsky, 2010a). Photochemistry predicts a constant HCl mixing ratio at 70 to ~90 km (Krasnopolsky, 2012), and a small difference in the altitudes for HCl and DCI may be neglected. Then the observed DCI/HCl ratio is 280 ± 110 times the terrestrial D/H near 75 km on Venus.

The calculated structure of the spectral feature at 2141.48 cm\(^{-1}\) is shown in Fig. 3. It is mostly formed by three CO2 lines and one CO line from Venus and the telluric H2O line. The solar spectrum is flat within this feature, and the DCI line contributes 5% to its equivalent width.

2.3. Discussion

There are two regions of significant exchange of deuterium be-
tween H2O, HCl, and H2 on Venus: the mesosphere and the hot
atmosphere near the surface.

A net effect of the chlorine chemistry in the mesosphere is
2\(\text{HCl} + \text{SO}_2 + \text{CO}_2 \rightarrow \text{SO}_2\text{Cl}_2 + \text{H}_2\text{O} + \text{CO}\)
with a global-mean rate of 1.9 × 10^9 cm\(^{-2}\) s\(^{-1}\) (Krasnopolsky, 2012). The HCl column photolysis rate exceeds that of H2O by a factor of 70, though the photolysis of H2O dominates above 100 km. Photol-
ysis frequencies for HDO and DCI are significantly smaller than
those of H2O and HCl, respectively (Liang and Yung, 2008). There-
fore the above process is depleted for DCI and results in an enrich-
ment of D in HCl and depletion in H2O in the mesosphere. This fractionation of deuterium between HCl and H2O is stronger than that by nonthermal escape of H and D (Gurwell and Yung, 1993; Donahue, 1999) by two orders of magnitude. However, contrary to the nonthermal escape, this fractionation does not change the total deuterium abundance in the atmosphere.

The calculated SO2Cl2 mixing ratio reaches a maximum of
35 ppb at 66 km (Krasnopolsky, 2012), and this reduces the HCl mixing ratio in that model from 400 ppb at the lower boundary of
47 km to 330 ppb at 66 km. (This reduction is small and poorly seen in Fig. 6 in Krasnopolsky (2012).) If the reduction refers only
to HCl and does not affect DCI, then the proper increase in the DCI/
HCl ratio is a factor of 1.21. This factor is rather similar to the ob-
served ratio of \(\text{(D/H)}\text{HCl} \approx 280\) to \(\text{(D/H)}\text{HDO} \approx 240\) (Fedorova et al., 2008) that is equal to 1.17.

Even smaller HCl abundances of ~150 ppb were observed at
70–105 km by the SOIR occultations at Venus Express (Vandaele et al., 2008). However, their data near 70 km disagree with the ground-based observations (Connes et al., 1967; Young, 1972; Krasnopolsky, 2010a), and the significant decrease in the HCl mixing ratio above the clouds is not supported by the model.

Fractionation of D/H in H2O may be also caused by formation of the sulfuric acid clouds. However, we have not found any data on this fractionation in the literature.

Thermodynamic equilibrium of
\[\text{HDO} + \text{H}_2 = \text{H}_2\text{O} + \text{HD}\]
in the lower atmosphere has a constant of 0.71 for the conditions
near the surface (92 bar, 735 K). It was calculated using the thermo-
dynamic data from Chase (1998). Then
\[\text{HD} / \text{H}_2 = 0.71 \text{HDO} / \text{H}_2\text{O}\]
if thermodynamic equilibrium is applicable. A similar approach to DCI results
HDO + HCl = H$_2$O + DCI
with the equilibrium constant of 0.37 and DCI/HCl = 0.37 HDO/H$_2$O, that is,

\[(D/H)_{\text{HCl}} = 0.74(D/H)_{\text{H}_2\text{O}}\]

and is similar to (D/H)$_{\text{H}_2}$.

Therefore, the enrichment of HCl in deuterium relative to H$_2$O occurs in the mesosphere, the enriched DCI is transported into the lower atmosphere and passes D to H$_2$O near the surface. A rate coefficient of the reaction between DCI and H$_2$O is 0.37 = 2.7 times that of HDO and HCl. The latter is unknown but may be similar to the rate coefficient of HDO + H$_2$, $k = 2 \times 10^{-22}$ e$^{-5170/7}$ cm$^3$ s$^{-1}$ (Lecluse and Robert, 1994). Then a time to establish equilibrium between D/H in HCl and H$_2$O near the surface is $\tau = (2.7k[H_2O])^{-1} = 2.5$ years. Here the H$_2$O mixing ratio is adopted at 30 ppm (Pollack et al., 1993; Bezzard et al., 2011). This time is rather short and comparable to the mixing time $\tau_{\text{in}} = H^2/k = 3$ years in the lower atmosphere, where eddy diffusion $K$ is $\sim 10^4$ cm$^2$ s$^{-1}$. The exchange of D becomes ineffective above $\sim 15$ km because of the lower temperature and the high activation energy.

These considerations are qualitative and may be insufficient to explain the observed increase in (D/H)$_{\text{H}_2\text{O}}$ from the lower atmosphere to the mesosphere by a factor of 2. Comparison of the chemical and mixing times favors a constant HDO/H$_2$O up to $\sim 100$ km and D/H in HCl equal to that in H$_2$O times 0.74. While the latter is within the uncertainty of DCI/HCl = 280 $\pm$ 110, the former disagrees with the HDO/H$_2$O observations at the various levels in the Venus atmosphere.

3. Search for NH$_3$ at the Venus cloud tops

3.1. Thermodynamic equilibrium for NH$_3$

Ammonia is a dominant form of nitrogen in the outer planets, comets, and interstellar clouds. Its abundance in the Venus lower atmosphere may be estimated from the following thermochemical equilibrium near the surface:

$$N_2 + 3H_2O + 3CO = 2NH_3 + 3CO_2$$

The equilibrium constant is calculated at $K = 10^{-2.15}$ using thermodynamic data from Chase (1998). Then

$$K = \frac{f_{\text{NH}_3} f_{\text{CO}_2} f_{\text{H}_2O}}{f_{\text{N}_2} f_{\text{CO}} f_{\text{H}_2}} 90^2$$

Here $f_x$ is the mixing ratio of X, and 90 bar is the surface pressure. Substituting $f_{\text{NH}_3} = 0.035, f_{\text{H}_2O} = 3 \times 10^{-5}$ (Pollack et al., 1993; Bezzard et al., 2011), and $f_{\text{CO}} = 1.4 \times 10^{-5}$ (Krasnopolsky, 2007b), one finds the NH$_3$ mixing ratio of $10^{-14}$.

A similar calculation for the NO mixing ratio from the thermochemical equilibrium

$$N_2 + 2CO_2 = 2NO + 2CO$$

results in $f_{\text{NO}} = 2 \times 10^{-18}$, much smaller than the observed value of $5.5 \times 10^{-19}$ (Krasnopolsky, 2006). Evidently NO is a disequilibrium species that is formed by lightning on Venus. However, the rather abundant NO may affect the abundance of NH$_3$ via the equilibrium:

$$2NO + 3H_2O + 5CO = 2NH_3 + 5CO_2$$

The calculated equilibrium constant is $K = 10^{43.0}$ at 735 K and results in the ammonia abundance of $6 \times 10^{-7}$ near the surface of Venus. One may expect that the NH$_3$ mixing ratio in the lower atmosphere of Venus is between these limiting values of $10^{-14}$ and $6 \times 10^{-7}$. Photochemical production of NH$_3$ is ineffective on Venus.

3.2. Observed spectrum and upper limit to NH$_3$

The most restrictive upper limit to ammonia at the cloud tops was established at 30 ppb by Kuiper (1969). Laboratory experiments by Titov (1983) showed that formation and condensation of ammonia pyrosulfite in the reaction

$$2NH_3 + 2SO_2 + H_2O \rightarrow (NH_4)_2S_2O_3$$

are possible even under this upper limit in cold regions at the cloud tops, and this species may contribute to the near UV absorption. Krasnopolsky (1986, p. 156) pointed out that ammonia pyrosulfite cannot be the main NUV absorber; otherwise strong anticorrelation would exist between the Pioneer Venus maps at 365 nm and 11.5 $\mu$m.

To search for NH$_3$ at the Venus cloud tops, we chose its strong line at 4484.11 cm$^{-1}$ with strength of $1.5 \times 10^{-20}$ cm at 230 K. The observation and data processing have been discussed in Section 1. The final spectrum is shown in Fig. 4. Its main features are the lines of the rare isotope $^{13}C^{16}O^{18}O$, which fraction in CO$_2$ is $4.4 \times 10^{-5}$. The lines are Doppler-shifted to the red by 0.195 cm$^{-1}$. The other features are telluric methane lines. The expected Doppler-shifted position of the NH$_3$ line is also shown in Fig. 4.

Fitting to the measured spectrum at 4483.3–4485.0 cm$^{-1}$ by a synthetic spectrum is depicted in Fig. 5. The observed spectrum is adjusted for two wavenumber corrections and a variation of a product of the instrument sensitivity and Venus’ reflectivity. This variation is simulated by a cubic polynomial, that is, six parameters are applied to the spectrum. The synthetic spectrum is calculated using the CO$_2$ column abundance and its mean temperature on Venus and three parameters for the telluric CH$_4$ (abundance, mean temperature and pressure). It is convolved by the instrument response function that is a Gaussian with dispersion as a free parameter. The CO$_2$ lines on Venus are calculated using the Voigt formulation, and the CH$_4$ lines in the Earth’s atmosphere are fitted by the integrated absorption from Krasnopolsky et al. (1997):

$$\tau_v = \frac{\mu SN}{4\pi v} \ln \left[ 1 + \left( \frac{2\delta v}{v - v_0} \right)^2 \right]$$

Here $\tau_v$ is the optical depth at wavenumber v, $\mu$ is the airmass, N is the column abundance, S is the line strength, and $\delta v$ is the collisional line halfwidth at the mean pressure and temperature. This
relationship was derived for an isothermal atmosphere and a constant mixing ratio of an absorber.

Standard deviation of the difference between the observed and synthetic spectra is scaled by a factor of $((44-1)/(44-12))^2 = 1.16$ to account for 12 fitting parameters; there are 44 pixels in the spectrum in Fig. 5. The difference spectrum has two broad features at 4483.9–4484.3 cm$^{-1}$ and 4484.3–4484.6 cm$^{-1}$ that involve 10 and 8 pixels, respectively. Probability of a random feature with 10 pixels of the same sign in this fitting is equal to $(44-10)/2^{10-1} = 0.066$. Therefore these features indicate some systematic errors in the fitting that exceed the noise. The corrected standard deviation results in a two-sigma upper limit of $5.2 \times 10^{-6}$ cm$^{-1}$ to the NH$_3$ line equivalent width. The line strength is $1.5 \times 10^{-20}$ cm, and an upper limit to the mean product of the NH$_3$ column abundance and the two-way airmass is $3.5 \times 10^{16}$ cm$^{-2}$. Our observations of the CO$_2$ lines near 4444 cm$^{-1}$ in the similar geometry resulted in this product of $\sim 370$ mbar (Krasnopolsky 2010a). 1 mbar $= 1.52 \times 10^{22}$ cm$^{-2}$ near the cloud tops, and the two-sigma upper limit is 6 ppb for NH$_3$ at the Venus cloud tops.

This is an improvement of the previous upper limit by a factor of 5. The derived upper limit is within the range of $10^{-14}$ to $6 \times 10^{-7}$ established for the thermodynamic equilibriums for NH$_3$. If ammonia is present in the atmosphere of Venus at the ppb level or less, it quickly dissociates above the clouds and weakly affects the atmospheric photochemistry.

4. Conclusions

To search for DCI in the Venus atmosphere, we observed a spectrum near the D$^2$Cl (1–0) R4 line at 2141.54 cm$^{-1}$ using the CSHELL spectrograph at NASA IRTF. Least square fitting to the observed spectrum results in a DCI mixing ratio of $17.8 \pm 6.8$ ppb. Comparing to the HCl abundance of 400 $\pm$ 30 ppb (Krasnopolsky, 2010a), the DCI/HCl ratio is equal to 280 $\pm$ 110 times the terrestrial D/H = 1.56 $\times$ $10^{-4}$. This ratio is similar to that of HDO/ H$_2$O = 240 $\pm$ 25 from the VEX/SOIR occultations (Fedorova et al., 2008) at 70–110 km.

Photochemistry in the Venus mesosphere converts H from HCl to that in H$_2$O with a rate of $1.9 \times 10^8$ cm$^{-2}$s$^{-1}$. The conversion involves photoysis of HCl; therefore, the photochemistry tends to enrich D/H in HCl and deplete in H$_2$O. The enriched HCl moves down by mixing to the lower atmosphere, where thermodynamic equilibriums for H$_2$ and HCl near the surface correspond to D/H = 0.71 and 0.74 times that in H$_2$O, respectively. Time to establish these equilibriums is $\sim 3$ years and comparable to the mixing time in the lower atmosphere. Therefore, the enriched HCl from the mesosphere gives D back to H$_2$O near the surface. Comparison of chemical and mixing times favors a constant HDO/H$_2$O up to $\sim 100$ km and DCI/HCl equal to D/H in H$_2$O times 0.74.

Ammonia is an abundant form of nitrogen in reducing environments. Thermodynamic equilibriums with N$_2$ and NO near the surface of Venus give its mixing ratio of $10^{-14}$ and $6 \times 10^{-16}$, respectively. A spectrum of Venus near the NH$_3$ line at 4481.11 cm$^{-1}$ was observed at NASA IRTF and resulted in a two-sigma upper limit of 6 ppb for NH$_3$ above the Venus clouds. This is an improvement of the previous upper limit by a factor of 5. If ammonia exists at the ppb level or less in the lower atmosphere, it quickly dissociates in the mesosphere and weakly affects its photochemistry.

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