Observation of DCl and upper limit to NH$_3$ on Venus

Vladimir Krasnopolsky *,[1]

Department of Physics, Catholic University of America, Washington, DC 20064, USA
Moscow Institute of Physics and Technology, Dolgoprudnyy, Russia

ARTICLE INFO

ABSTRACT

To search for DCl in the Venus atmosphere, a spectrum near the D^{35}Cl (1–0) R4 line at 2141.54 cm^{-1} was observed using the CSHELL 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 D/H = 1.56 × 10^{-4}. This ratio is similar to that of HDO/H$_2$O = 240 ± 25 times the terrestrial HDO/H$_2$O from the VEX/SOIR occultations 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 × 10^9 cm^{-2} s^{-1} (Krasnopolsky [2012] Icarus, 218, 230–246). The conversion involves photolysis of HCl; therefore, the photochemistry tends to enrich D/H in HCl and deplete in H$_2$O. Formation of the sulfuric acid clouds may affect HDO/H$_2$O as well. 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 estimated at ~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 ~100 km and DCl/HCl equal to D/H in H$_2$O times 0.74.

Ammonia is an abundant form of nitrogen in the reducing environments. Thermodynamic equilibriums with N$_2$ and NO near the surface of Venus give its mixing ratio of 10^{-14} and 6 × 10^{-7}, 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.

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 0.0023v_0, where v_0 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^{-6}v_0 in the dispersion direction and 0.21 arcsec in the aspect direction. The instrument resolving power is $v/\delta v$ = 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 DCl and NH_3 spectra to get mean abundances of these species on Venus.

2. Search for DCl 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_2O was equal to 100 ± 15 times the terrestrial value of $HDO/H_2O = 3.11 \times 10^{-4}$ (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 μm; the retrieved D/H in H_2O 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_2O 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 μm. They assign the observed values to 62 km. Observations by Krasnopolsky (2010a) at 2.3 μm 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 μm while Krasnopolsky (2010a) considered the middle of the CO_2 layer with pressure smaller by a factor of 2. The H_2O abundance has not been observed by Matsui et al. (2012), and their D/H that was based on the adopted 5 ppm of H_2O is actually very uncertain because of the significant variations of H_2O. Measurements of the HDO/H_2O 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_2O ratio without simultaneous observations of H_2O.

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_2O, HCl, HDO, and DCl 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_2O and HDO (Cheng et al., 1999) and HCl and DCl (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 DCl 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 DCl.

2.2. Observed spectrum of DCl

The spectroscopic database HITRAN-2008 (Rothman et al., 2009) does not include DCl, and we searched for the DCl line wavenumbers and strengths in the literature. The HCl mixing ratio is 400 ppb at 74 km on Venus (Krasnopolsky, 2010a), and the expected DCl abundance is very small, 12.5 ppb for D/H ≈ 200. Therefore, we should use the strongest DCl 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 (Benedict 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 DCl R4 line at 2141.540 cm^{-1} is the best for the observation, though it is contaminated by CO_2, CO, and H_2O lines. Wavenumbers of the DCl lines are taken from Klee 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 $(1.51–1.45) \times 10^{-19}$ cm, and we will adopt $S = 1.47 \times 10^{-19}$ 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 μm (Crovisier et al., 2006). The other features are the absorption lines of CO_2 and CO from Venus, telluric lines of H_2O, and the solar lines. Weak telluric lines of CO_2, N_2O, and O_3 are present as well. The expected Doppler-shifted position of the DCl 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_2O 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 DCl abundances
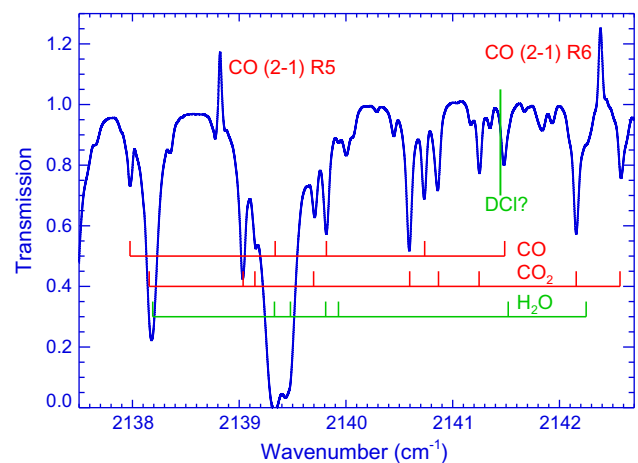

Fig. 1. Spectrum of Venus near the $D^{35}Cl$ R4 line of the (1–0) band. The expected position of the DCl line, strong Venus' CO and CO_2 and telluric H_2O lines are marked. The spectrum also includes two emission lines of the hot CO (2–1) band. All Venus lines are Doppler-shifted to the red by 0.093 cm^{-1}. Some weaker features are the solar lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
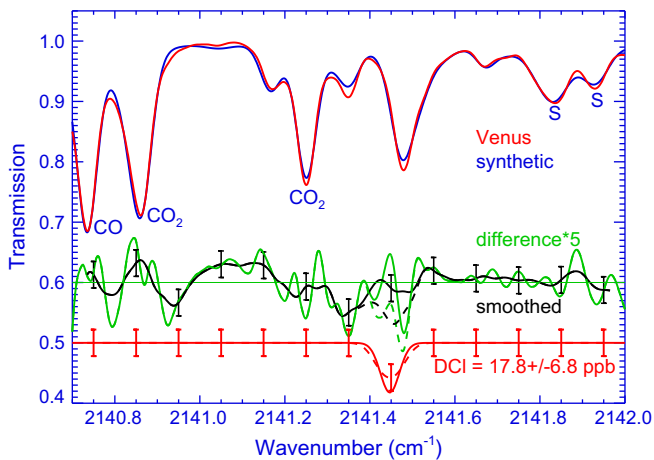
Fig. 2. A part of the spectrum from Fig. 1 (red) that is fitted by a synthetic spectrum (blue). Their differences with (solid) and without (dashed) DCl line are shown scaled by a factor of 5 (green). These differences smoothed within 0.07 cm^{-1} are black, and the unsmoothed and smoothed contributions of the DCl line are red. The error bars reflect standard deviation of the black curve corrected for the number of fitting parameters. The retrieved DCl line is scaled to the CO_2 lines to get a DCl 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.)

and their mean temperature in the Venus atmosphere above the clouds, H_2O abundance and fixed CO_2, N_2O, and O_3 abundances in the overhead Earth's atmosphere, and spectral resolution, two 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 H_2O mean temperature and pressure are fixed at 270 K and 0.5 bar, those for CO_2 and N_2O are 230 K and 0.3 bar (half total pressure and temperature at this level), and 230 K and 25 mbar for O_3.

The least square fit synthetic spectrum is shown in Fig. 2. Differences between the observed spectrum and the synthetic spectra with and without DCl 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 DCl 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 $((68-1)/(68-13))^{1/2} = 1.10$. Here 68 is the number of degrees of
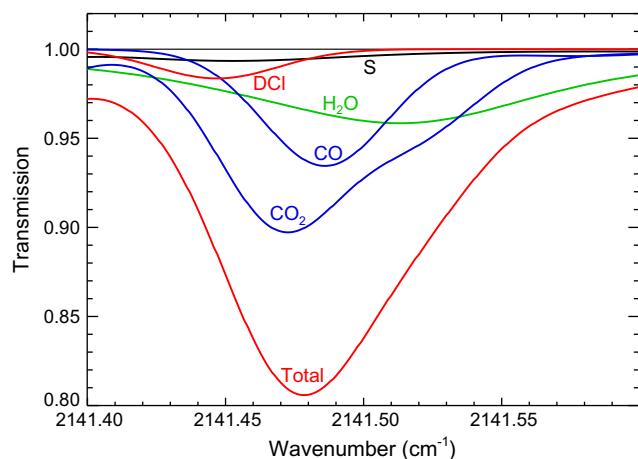
freedom (pixels) and 13 is the number of fitting parameters. This uncertainty is depicted as the error bars in Fig. 2.

The DCl abundance is directly scaled to CO_2 in our synthetic spectrum, and the best fit DCl mixing ratio is 17.8 ± 6.8 ppb. The uncertainty is actually a sum of noise in the observation and an uncertainty of the spectral fitting. The retrieved value is 2.6 sigmas, that is, slightly below the standard detection criterion of 3 sigmas. However, it may be of some interest and deserves discussion.

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 DCl may be neglected. Then the observed DCl/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 CO_2 lines and one CO line from Venus and the telluric H_2O line. The solar spectrum is flat within this feature, and the DCl line contributes 5% to its equivalent width.

2.3. Discussion

There are two regions of significant exchange of deuterium between H_2O, HCl, and H_2 on Venus: the mesosphere and the hot atmosphere near the surface.

A net effect of the chlorine chemistry in the mesosphere is

$$2HCl + SO_2 + CO_2 \rightarrow SO_2Cl2 + H_2O + CO$$
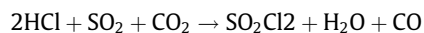
with a global-mean rate of 1.9×10^9 cm^{-2} s^{-1} (Krasnopolsky, 2012). The HCl column photolysis rate exceeds that of H_2O by a factor of 70, though the photolysis of H_2O dominates above 100 km. Photolysis frequencies for HDO and DCl are significantly smaller than those of H_2O and HCl, respectively (Liang and Yung, 2008). Therefore the above process is depleted for DCl and results in an enrichment of D in HCl and depletion in H_2O in the mesosphere. This fractionation of deuterium between HCl and H_2O 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 SO_2Cl_2 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 DCl, then the proper increase in the DCl/HCl ratio is a factor of 1.21. This factor is rather similar to the observed ratio of (D/H)$_{HCl} \approx 280$ to (D/H)$_{H2O} \approx 240$ (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 H_2O may be also caused by formation of the sulfuric acid clouds. However, we have not found any data on this fractionation in the literature.
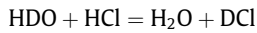
Thermodynamic equilibrium of

$$HDO + H_2 = H_2O + HD$$
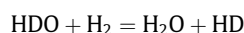
in the lower atmosphere has a constant of 0.71 for the conditions near the surface (92 bar, 735 K). It was calculated using the thermodynamic data from Chase (1998). Then

$$HD/H_2 = 0.71 HDO/H_2O$$

Fig. 3. Structure of the absorption feature at 2141.48 cm^{-1}. It consists of the telluric H_2O line and venusian lines of CO_2 (three lines), CO, and DCl. The latter is 5% of the total equivalent width. The solar spectrum S is almost flat within the feature.

if thermodynamic equilibrium is applicable. A similar approach to DCl results

$$HDO + HCl = H_2O + DCl$$

with the equilibrium constant of 0.37 and DCl/HCl = 0.37 HDO/H_2O, that is,

$$(D/H)_{HCl} = 0.74(D/H)_{H2O}$$

and is similar to $(D/H)_{H2}$.

Therefore, the enrichment of HCl in deuterium relative to H_2O occurs in the mesosphere, the enriched DCl is transported into the lower atmosphere and passes D to H_2O near the surface. A rate coefficient of the reaction between DCl and H_2O is $0.37^{-1} = 2.7$ times that of HDO and HCl. The latter is unknown but may be similar to the rate coefficient of HDO + H_2, $k = 2 \times 10^{-22}$ $e^{-5170/T}$ cm^3 s^{-1} (Lecluse and Robert, 1994). Then a time to establish equilibrium between D/H in HCl and H_2O near the surface is $\tau = (2.7k[H_2O])^{-1} = 2.5$ years. Here the H_2O mixing ratio is adopted at 30 ppm (Pollack et al., 1993; Bezard et al., 2011). This time is rather short and comparable to the mixing time $\tau_m = H^2/K \approx 3$ years in the lower atmosphere, where eddy diffusion K is $\sim 10^4$ cm^2 s^{-1}. The exchange of D becomes ineffective above ~ 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 $(D/H)_{H2O}$ from the lower atmosphere to the mesosphere by a factor of 2. Comparison of the chemical and mixing times favors a constant HDO/H_2O up to ~ 100 km and D/H in HCl equal to that in H_2O times 0.74. While the latter is within the uncertainty of DCl/HCl = 280 ± 110, the former disagrees with the HDO/H_2O 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

$$K = \frac{f_{NH3}^2}{f_{N2}f_{H2O}^3 f_{CO}^3 * 90^2}$$

Here f_X is the mixing ratio of X, and 90 bar is the surface pressure. Substituting $f_{N2} = 0.035$, $f_{H2O} = 3 \times 10^{-5}$ (Pollack et al., 1993; Bezard et al., 2011), and $f_{CO} = 1.4 \times 10^{-5}$ (Krasnopolsky, 2007b), one finds the NH_3 mixing ratio of 10^{-14}.

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

$$N_2 + 2CO_2 = 2NO + 2CO$$
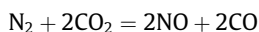
results in $f_{NO} = 2 \times 10^{-18}$, much smaller than the observed value of 5.5×10^{-9} (Krasnopolsky, 2006). Evidently NO is a disequilibrium species that is formed by lightning on Venus. However, the rather abundant NO may affect the abundance of NH_3 via the equilibrium:

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

The calculated equilibrium constant is $K = 10^{40.0}$ at 735 K and results in the ammonia abundance of 6×10^{-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 6×10^{-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

$$2NH_3 + 2SO_2 + H_2O \rightarrow (NH_4)_2S_2O_5$$
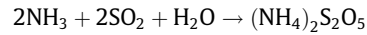
are possible even under this upper limit in cold regions at the cloud tops, and this species may contribute to the near UV absorption. Krasnopolsky (1986, p. 156) pointed out that ammonia pyrosulfite cannot be the main NUV absorber; otherwise strong anticorrelation would exist between the Pioneer Venus maps at 365 nm and 11.5 μm.

To search for NH_3 at the Venus cloud tops, we chose its strong line at 4484.11 cm^{-1} with strength of 1.5×10^{-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 4.4×10^{-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):

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

Here τ_v is the optical depth at wavenumber v, μ is the airmass, N is the column abundance, S is the line strength, and δv is the collisional line halfwidth at the mean pressure and temperature. This
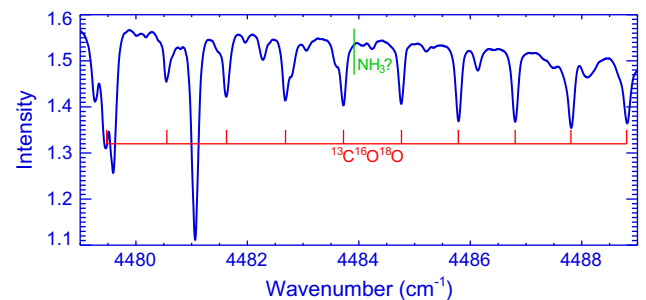

Fig. 4. Spectrum of Venus near the NH_3 line at 4484.11 cm^{-1}. Main features are the $^{13}C^{16}O^{18}O$ absorption lines and telluric H_2O lines. The $^{13}C^{16}O^{18}O$ lines and the expected position of the NH_3 line are Doppler-shifted to the red by 0.195 cm^{-1}. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
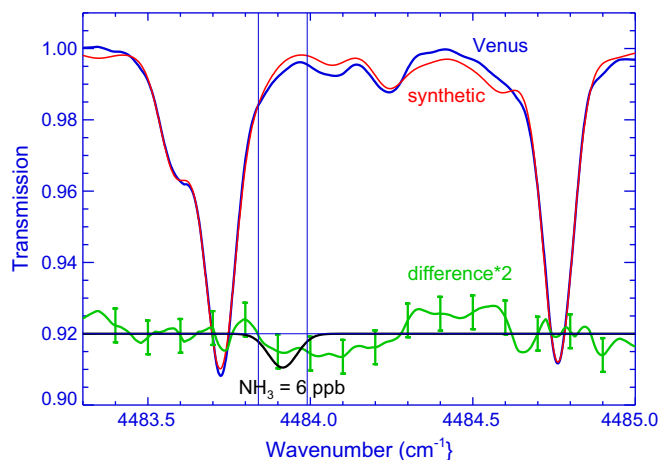
Fig. 5. A part of the spectrum from Fig. 4 (blue) that is chosen to fit by a synthetic spectrum (red). Their difference scaled by a factor of 2 is green, and the error bars are standard deviation of the green curve corrected for the number of fitting parameters. The vertical lines show an interval of 0.15 cm^{-1} at the expected Doppler-shifted position of the NH_3 line. Calculated absorption line of NH_3 for its mixing ratio of 6 ppb (black) corresponds to the 2σ upper limit. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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 $((44-1)/(44-12))^{1/2} = 1.16$ 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 5.2×10^{-4} cm^{-1} to the NH_3 line equivalent width. The line strength is 1.5×10^{-20} cm, and an upper limit to the mean product of the NH_3 column abundance and the two-way airmass is 3.5×10^{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 = 1.52×10^{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 6×10^{-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 DCl in the Venus atmosphere, we observed a spectrum near the $D^{35}Cl$ (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 DCl mixing ratio of 17.8 ± 6.8 ppb. Comparing to the HCl abundance of 400 ± 30 ppb (Krasnopolsky, 2010a), the DCl/HCl ratio is equal to 280 ± 110 times the terrestrial D/H = 1.56×10^{-4}. This ratio is similar to that of HDO/H_2O = 240 ± 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_2O with a rate of 1.9×10^9 cm^{-2} s^{-1}. The conversion

involves photolysis of HCl; therefore, the photochemistry tends to enrich D/H in HCl and deplete in H_2O. 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_2O, 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_2O near the surface. Comparison of chemical and mixing times favors a constant HDO/H_2O up to $\sim$100 km and DCl/HCl equal to D/H in H_2O 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 6×10^{-7}, 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.

References

Bahou, M., Chung, C.Y., Lee, Y.P., Cheng, B.M., Yung, Y.L., Lee, L.C., 2001. Absorption cross sections of HCl and DCl at 135–232 nanometers: Implications for photodissociation on Venus. Astrophys. J. 559, L179–L182.

Benedict, W.S., Herman, R., Moore, G.E., Silverman, S., 1957. Infrared line and band strengths and dipole momentum function in HCl and DCl. J. Chem. Phys. 26, 1671–1679.

Bezard, B., Fedorova, A., Bertaux, J.L., Rodin, A., Korablev, O., 2011. The 1. 10- and 1.18-μm nightside windows of Venus observed by SPICAV-IR aboard Venus Express. Icarus 216, 173–183.

Bjoraker, G.L., Larson, H.P., Mumma, M.J., Timmermann, R., Montani, J.L., 1992. Airborne observations of the gas composition of Venus above the cloud tops: Measurements of H_2O, HDO, HF and the D/H and $^{18}O/^{16}O$ isotope ratios. Bull. Am. Astron. Soc. 24, 995 (abstract).

Chase Jr., M.W., 1998. NIST-JANAF Thermodynamic Tables. fourth ed. J. Phys. Chem. Ref. Data Monograph 9.

Cheng, B.M., Chew, E.P., Liu, C.P., Bahou, M., Lee, Y.P., Yung, Y.L., Gerstell, M.F., 1999. Photo-induced fractionation of water isotopomers in the martian atmosphere. Geophys. Res. Lett. 26, 3657–3660.

Connes, P., Connes, J., Benedict, W.S., Kaplan, L.D., 1967. Traces of HCl and HF in the atmosphere of Venus. Astrophys. J. 147, 1230–1237.

Crovisier, J., Lellouch, E., de Bergh, C., Maillard, J.P., Lutz, B.L., Bezard, B., 2006. Carbon monoxide emissions at 4.7 μm from Venus' atmosphere. Planet. Space Sci. 54, 1398–1414.

De Bergh, C., Bezard, B., Owen, T., Crisp, D., Maillard, J.P., Lutz, B.L., 1991. Deuterium on Venus: Observations from Earth. Science 251, 547–549.

Donahue, T.M., 1999. New analysis of hydrogen and deuterium escape from Venus. Icarus 141, 226–235.

Donahue, T.M., Hoffman, J.H., Hodges, R.R., Watson, A.J., 1982. Venus was wet: A measurement of the ratio of D to H. Science 216, 630–633.

Encrenaz, Th., Lellouch, E., Cernicharo, J., Paubert, G., Gulkis, S., Spilker, T., 1995. The thermal profile and water abundance in the Venus mesosphere from H_2O and HDO millimeter observations. Icarus 117, 162–172.

Fedorova, A. et al., 2008. HDO and H_2O vertical distributions and isotopic ratio in the Venus mesosphere by Solar Occultation at Infrared spectrometer on board Venus Express. J. Geophys. Res. 113, E00B22.

Gurwell, M.A., Yung, Y.L., 1993. Fractionation of hydrogen and deuterium on Venus due to collisional ejection. Planet. Space Sci. 41, 91–104.

Hartle, R.E., Taylor, H.A., 1983. Identification of deuterium ions in the ionosphere of Venus. Geophys. Res. Lett. 10, 965–968.

Hase, F., Wallace, L., McLeod, S.D., Harrison, J.J., Bernath, P.F., 2010. The ACE-FTS atlas of the infrared solar spectrum. J. Quant. Spectrosc. Radiat. Trans. 111, 521–528.

Klee, S., Ogilvie, J.F., 1993. The fundamental vibration-rotational band of gaseous DCl in absorption at 297 K and at 12 K. Spectrochim. Acta 49A, 345–355.

Krasnopolsky, V.A., 1986. Photochemistry of the Atmospheres of Mars and Venus. Springer-Verlag, New York.

Krasnopolsky, V.A., 2006. A sensitive search for nitric oxide in the lower atmospheres of Venus and Mars: Detection on Venus and upper limit for Mars. Icarus 182, 80–91.

Krasnopolsky, V.A., 2007a. Long-term spectroscopic observations of Mars using IRTF/CSHELL: Mapping of O_2 dayglow, CO, and search for CH_4. Icarus 190, 93–102.

Krasnopolsky, V.A., 2007b. Chemical kinetic model for the lower atmosphere of Venus. Icarus 191, 25–37.

Krasnopolsky, V.A., 2010a. Spatially-resolved high-resolution spectroscopy of Venus. 1. Variations of CO_2, CO, HF, and HCl at the cloud tops. Icarus 208, 539–547.

Krasnopolsky, V.A., 2010b. Spatially-resolved high-resolution spectroscopy of Venus. 2. Variations of HDO, OCS, and SO_2 at the cloud tops. Icarus 209, 314–322.

Krasnopolsky, V.A., 2012. A photochemical model for the Venus atmosphere at 47–112 km. Icarus 218, 230–246.

Krasnopolsky, V.A., Bjoraker, G.L., Mumma, M.J., Jennings, D.E., 1997. High-resolution spectroscopy of Mars at 3.7 and 8 μm: A sensitive search for H_2O_2, H_2CO, HCl, and CH_4, and detection of HDO. J. Geophys. Res. 102, 6525–6534.

Kuiper, G.P., 1969. Identification of the Venus cloud layers. Commun. Lunar Planet. Lab. 6, 229–250.

Lecluse, C., Robert, F., 1994. Hydrogen isotope exchange reaction rates: Origin of water in the inner Solar System. Geochim. Cosmochim. Acta 58, 2927–2939.

Liang, M., Yung, Y.L., 2009. Modeling the distribution of H_2O and HDO in the upper atmosphere of Venus. J. Geophys. Res. 114, E00B28.

Matsui, H., Iwagami, N., Hosouchi, M., Ohtsuki, S., Hashimoto, G.I., 2012. Latitudinal distribution of HDO abundance above Venus' clouds by ground-based 2.3 μ spectroscopy. Icarus 217, 610–614.

McElroy, M.B., Prather, M.J., Rodriguez, J.M., 1982. Escape of hydrogen from Venus. Science 215, 1614–1615.

Pollack, J.B. et al., 1993. Near-infrared light from Venus' nightside: A spectroscopic analysis. Icarus 103, 1–42.

Rothman, L.S. et al., 2009. The HITRAN 2008 molecular spectroscopic database. J. Quant. Spectrosc. Radiat. Trans. 110, 533–572.

Sandor, B.J., Clancy, R.T., 2005. Water vapor variations in the Venus mesosphere from microwave spectra. Icarus 177, 129–143.

Titov, D.V., 1983. On the possibility of aerosol formation by the reaction between SO_2 and NH_3 in the Venus atmosphere. Cosmic Res. 21, 401–408.

Vandaele, A.C. et al., 2008. Composition of the Venus mesosphere measured by Solar Occultation at Infrared on board Venus Express. J. Geophys Res. 113, E00B23.

Young, L.D.G., 1972. High resolution spectra of Venus: A review. Icarus 17, 632–658.