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Spatially-resolved high-resolution spectroscopy of Venus
1. Variations of CO_2, CO, HF, and HCl at the cloud tops

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A B S T R A C T

Variations of the upper cloud boundary and the CO, HF, and HCl mixing ratios were observed using the CSHELL spectrograph at NASA IRTF. The observations were made in three sessions (October 2007, January 2009, and June 2009) at early morning and late afternoon on Venus in the latitude range of ±60°. CO_2 lines at 2.25 μm reveal variations of the cloud aerosol density (∼25%) and scale height near 65 km. The measured reflectivity of Venus at low latitudes is 0.7 at 2.25 μm and 0.028 at 3.66 μm, and the effective CO_2 column density is smaller at 3.66 μm than those at 2.25 μm by a factor of 4. This agrees with the almost conservative multiple scattering at 2.25 μm and single scattering in the almost black aerosol at 3.66 μm. The expected difference is just a factor of $(1-g)^{-1} = 4$, where $g = 0.75$ is the scattering asymmetry factor for Venus' clouds. The observed CO mixing ratio is 52 ± 4 ppm near 08:00 and 40 ± 4 ppm near 16:30 at 68 km, and the higher ratio in the morning may be caused by extension of the CO morningside bulge to the cloud tops. The observed weak limb brightening in CO indicates an increase of the CO mixing ratio with altitude. HF is constant at 3.5 ± 0.2 ppb at 68 km in both morningside and afternoon observations and in the latitude range ±60°. Therefore the observations do not favor a bulge of HF, though HF is lighter than CO. Probably a source in the upper atmosphere facilitates the bulge formation. The recent measurements of HCl near 70 km are controversial (0.1 and 0.74 ppm) and require either a strong sink or a strong source of HCl in the clouds. The HCl lines of the (2-0) band are blended by the solar and telluric lines. Therefore we observed the P8 lines of the (1-0) band at 3.44 μm. These lines are spectrally clean and result in the HCl mixing ratio of 0.40 ± 0.03 ppm at 74 km. HCl does not vary with latitude within ±60°. Our observations support a uniformly mixed HCl throughout the Venus atmosphere.

1. Introduction

High-resolution infrared spectroscopy is a powerful tool to study chemical composition of the planetary atmospheres. High-resolution spectra of Venus, Mars, Jupiter, and Saturn were observed for the first time in the pioneering work by Connes et al. (1969) using their Fourier transform spectrometer (FTS). The spectra of Venus were measured with the unprecedented resolving power $\nu/\delta\nu \approx 10^5$ and resulted in the first detections of HCl, HF, and CO (Connes et al., 1967, 1968).

Kuiper et al. (1969) and Fink et al. (1972) made the first reliable observations of H_2O on Venus using an FTS at an airborne observatory. (Column density of H_2O above Venus' clouds is ∼1 precipitable μm, lower than that on Mars by an order of magnitude, and poorly accessible to the ground-based infrared astronomy.)

High-resolution spectra of the nightside thermal emissions at 1.74 and 2.3 μm were observed by Bezard et al. (1990) and resulted in the first reliable detection of OCS that refers to the lower atmosphere near 33 km. Absorption lines of CO_2, CO, SO_2, H_2O, HDO, HCl, and HF were detected as well. That was the first spectroscopic determination of the D/H ratio (de Bergh et al., 1991); previous measurements of D/H on Venus were based on the Pioneer Venus mass spectrometers (Donahue et al., 1982; Hartle and Taylor, 1983). The observed spectra along with some medium resolution observations were analyzed by Pollack et al. (1993), Taylor et al. (1997) and Bezard and de Bergh (2007) to retrieve abundances of the above species in the lower atmosphere of Venus and their variations with altitude.

Venus was observed at 2.6 μm using an FTS at the Kuiper Airborne Observatory (Bjoraker et al., 1992). Absorption lines of H_2O, HDO, HF, and CO_2 were measured; $H_2{}^{18}O$ was detected for the first time on Venus.

The most sensitive search for O_2 on Venus was made by Trauger and Lunine (1983) who established an upper limit of 10^{18} cm^{-2}

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above the clouds (see Krasnopolsky, 2006b). They used a triple pressure-scanning Fabry–Perot interferometer with resolving power of 2.4×10^5. Photons were collected from the full Venus disk by that instrument, and the signal-to-noise ratio was very high. This important result has not been improved for the last quarter of century.

Due to a progress in the multielement detector arrays, high-resolution long-slit echelle spectrographs have been built and replaced the FTS's at astronomical observatories. These spectrographs have lower resolving power than the FTS's but make feasible spatially resolved and mapping observations. Spectra of all points along the slit are measured, and species abundances may be extracted at all those points.

NO was detected for the first time at the Venus cloud tops (Krasnopolsky, 2006a) using the TEXES spectrograph (Lacy et al., 2002). That was a convincing proof of lightning on Venus. Recently OCS at the cloud tops was detected (Krasnopolsky, 2008, hereafter Paper I) using the CSHELL spectrograph (Greene et al., 1993). Both detections were made at the NASA Infrared Telescope Facility (IRTF) on Hawaii.

High-resolution spectroscopy significantly contributed to study of the Venus night airglow. The O_2 nightglow at 1.27 μm was detected by Connes et al. (1979) using FTS. Slanger et al. (2001) detected the oxygen green line at 558 nm in Venus nightglow using the HIRES spectrograph at the Keck Observatory. Recently the OH nightglow, which was detected by Venus Express (Piccioni et al., 2008), was observed using CSHELL (Krasnopolsky, 2010).

High-resolution spectrographs are complicated and heavy, and this hindered them at spacecraft missions to the planets. The SOIR at Venus Express is probably the first and only exception here. SOIR is observing vertical profiles of CO, HCl, HF, H_2O, HDO, and SO_2 above 70 km in the solar occultation mode (Bertaux et al., 2007; Fedorova et al., 2008; Vandaele et al., 2008; Belyaev et al., 2008).

The SOIR observations are restricted by the Venus Express orbit geometry, and almost all published data refer to the north polar regions above 60°N. Only two SO_2 observations were made at low latitudes, 23 and 30°N. Therefore spatially-resolved high-resolution ground-based observations may complement the Venus Express data. Our goal is to study variations of minor constituents of the Venus atmosphere with latitude, local time, and from place to place. Some data from the first session have been published in Paper I, and the current paper is a continuation of that work.

2. Observations

We have observed Venus at three sessions using CSHELL at NASA IRTF. CSHELL is a high-resolution long-slit echelle spectrograph for the near infrared range of 1–5.5 μm. A spectral interval within this range may be chosen by varying angles of the diffraction grating and the circular variable filter. It is rather narrow and equal to $0.0023\nu_0$, where ν_0 is the central wavenumber. Therefore ν_0 should be carefully chosen. The instrument has an InSb detector array of 256 spectral to 150 spatial elements. Each pixel is $9 \times 10^{-6}\nu_0$ in the spectral direction and 0.2 arcsec in the spatial direction. The array is cooled to 30 K. Some parts of the instruments are also cooled. The instrument resolving power is $\nu/\delta\nu = 4 \times 10^4$ with a slit of 0.5 arcsec, that is, a resolution element is 2.8 pixels FWHM (full width at half maximum). Spatial resolution of the telescope–spectrograph combination is typically 1 arcsec.

NASA IRTF has a telescope with diameter of 3 m that is sufficient for many Solar System studies. The observatory is on the summit of Mauna Kea, Hawaii, with elevation of 4.2 km, pressure 0.6 bar, and typical overhead water of 2 pr. mm. These values are probably the best for the ground-based astronomy and facilitate detection of weak absorptions in planetary spectra.

We have had three sessions to observe Venus on October 18, 2007, January 13, 2009, and June 20, 2009. Venus was near its maximal solar elongation of ~45° in all our observations. Phase (Sun–planet-observer) angle is ~90° at this position, and this geometry is convenient for observations of both day and nightsides. Doppler shifts from geocentric velocity of Venus are maximal at ±13 km s^{-1} as well, improving the detection conditions relative to the telluric lines. The Venus size of 20–25 arcsec at these positions is also optimum for observations with the CSHELL slit of 30 arcsec. Usually we place the instrument slit parallel to the central meridian and at the middle of the illuminated part of the disk in our dayside observations. Then the observations cover a latitude range of ±60° and refer to local time of either 08:00 or 16:00, making therefore possible studying of variations with latitude and local time. Actually local time varies along the slit in our geometry, and local times mentioned here and below refer to the low latitudes. We also observed the instrument dark current, flat fields, the sky foreground, and standard infrared stars for calibration. Our observations and analysis of the Venus night airglow (Krasnopolsky, 2010) will not be considered here.

3. CO_2 lines and the upper cloud layer

Light scattering in absorption lines is rather complicated in the Venus clouds, and the best way to get a mixing ratio of an absorbing species is to measure CO_2 lines in the nearby spectral range. Many uncertainties in the retrieved column densities of the species and CO_2 cancel out in their ratio, especially if equivalent widths of the lines are similar. Therefore the chosen CO_2 lines should be rather weak. For example, if a CO line strength is $\sim 10^{-22}$ cm and the expected CO mixing ratio is ~40 ppm, then a desirable CO_2 line strength is $\sim 4 \times 10^{-27}$ cm.

Venus dayside is bright, exposures are short in our observations, and a typical interval between the observations of a species and CO_2 is ~30 min. Using the four-day rotation of Venus, this time is converted to the meridional shift of 2°, that is, 0.35 arcsec for the Venus diameter 20–25 arcsec. This shift is smaller than the spatial resolution of 1 arcsec, and the observations of a species and CO_2 may be considered as almost simultaneous.

3.1. CO_2 lines at 2.25 μm and variations of the upper clouds

We observed the CO_2 lines near 4444 cm^{-1} (Fig. 1, lower panel) for comparison with CO, HF, OCS, and the (2-0) band of HCl. High-resolution solar spectra observed by the ATMOS (Farmer and Norton, 1989) spacecraft cover this region and help to avoid contamination by the solar lines. We use a version of the ATMOS spectrum suggested by Kurucz (2009). Of six CO_2 lines in the spectrum two lines, R32 and R34, are rather clean at the negative Doppler shift. The R30 and R36 lines are better at the positive Doppler shift, and a minor contamination of R36 by a CH_4 telluric line is corrected using the nearby CH_4 lines in the spectrum.

Similar to the other spectroscopic studies cited in Section 1, we apply a simple reflection model. Multiple scattering in the clouds is substituted in this model by reflection at an effective level in the atmosphere. To find this effective level for each point along the chord on the Venus disk, we measure equivalent widths of the CO_2 lines in the spectrum. Then we calculate the equivalent width of the CO_2 line as a function of height by integration from 90 down to 60 km. We use the temperature and pressure profiles from the Venus International Reference Atmosphere (VIRA; Seiff et al., 1985) at latitude 45°. According to VIRA, latitudinal variations of temperature are ~3 K near 65–75 km, where the lines form, and weakly affect our results. The CO_2 line strengths and collisional self-broadened line widths for various temperatures are taken from the HITRAN 2008 spectroscopic database (Rothman et al.,

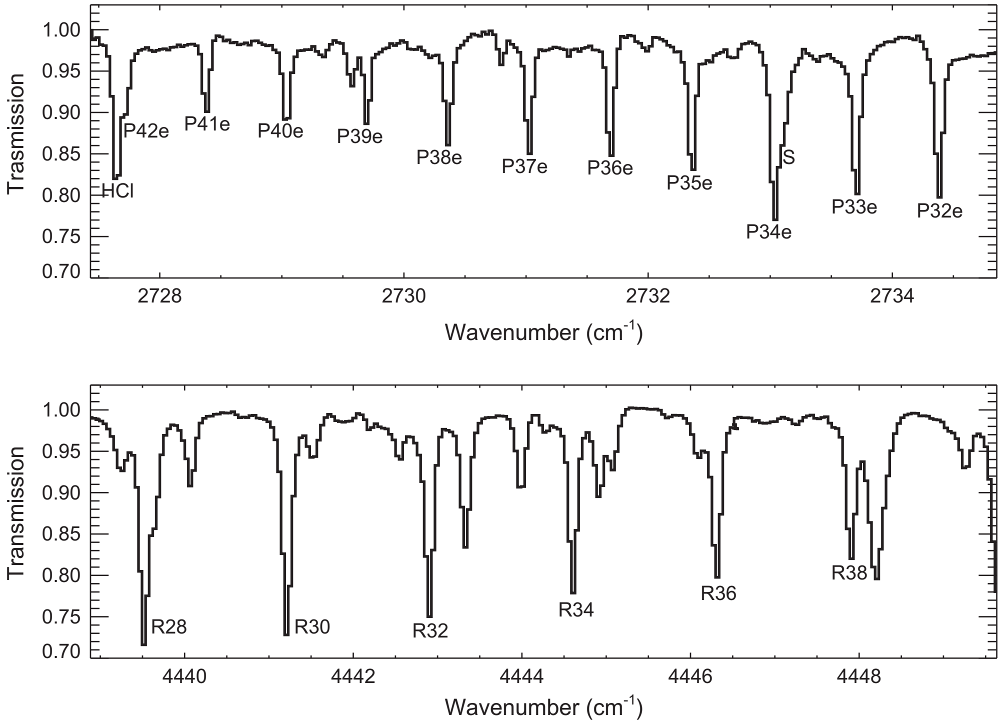

Fig. 1. CO_2 spectra observed in June 2009. Lower panel: CO_2 lines near 2.25 μm. Other features are the telluric CH_4 and solar lines. The CO_2 and solar lines are Doppler-shifted by $-0.201\ cm^{-1}$. Upper panel: $CO^{18}O$ lines near 3.66 μm. The HCl P7 line and a solar line that are blended with the CO_2 P42e and P34e lines are marked. The $CO^{18}O$, HCl, and solar lines are Doppler-shifted by $-0.124\ cm^{-1}$. Other weak lines are telluric CH_4, H_2O, and solar lines.

2009). We adopt the Voigt line shape that combines thermal and collisional broadening to calculate absorptions in 600 points of the line shape spaced by $10^{-3}\ cm^{-1}$. As in Paper I, the integration is made for the incidence and viewing angles at the observational point. The calculated equivalent width is equal to the observed value at the effective level of the reflection model. The effective level is given by atmospheric pressure in mbars and altitude in kilometers. Atmospheric pressure is a product of its column mass and gravity acceleration and may be converted to the CO_2 column density using 1 mbar = 1.52×10^{22} molecules cm^{-2} near Venus cloud tops.

The retrieved CO_2 column densities and their products by airmass $m = 1/\cos z + 1/\cos \psi$ are shown in Fig. 2; z is the solar zenith angle, and ψ is the viewing angle. The effective reflection level at 2.25 μm is ∼100 mbar, that is, near 65 km. The mCO_2 values are helpful for comparison of the atmospheric and aerosol scale heights near the cloud tops: if the values show limb brightening, then the atmospheric scale height is larger than that of the aerosol and vise versa. mCO_2 is rather constant in both morningside observations. This means that the aerosol near the cloud tops is uniformly mixed in the atmosphere. mCO_2 in October 2007 is smaller by 25% than that in June 2009, indicating a denser aerosol in the clouds.

The CO_2 column density is almost constant in the afternoon on January 2009 (Fig. 2, lower panel). This behavior is typical of a gas layer above a reflecting surface. The mCO_2 values at 16:30 on January 2009 are similar to those at 08:00 on October 2007 in the latitude range of ±35°.

Variations of the upper cloud boundary with local time at latitudes 25–75°N were observed by the Fourier Spectrometer at the Venera 15 orbiter (Zasova et al., 2007). The upper cloud boundary is a level of $\tau = 1$ at 1218 cm^{-1} in their Fig. 17. The boundary is at ∼67 km at 08:00 and 16:00 and similar within ∼0.3 km up to 50°N. The boundary is at ∼64 and ∼62 km and the difference increases in the afternoon to 1.3 and 2.9 km at 55°N and 65°N, respectively.

VIRTIS/VEX observations of the CO_2 band at 1.6 μm reveal the cloud top altitude of 74 ± 1 km at the low and middle latitudes (Ignatiev et al., 2009). The CO_2 lines in our observations are much weaker than the basic lines of the band at 1.6 μm and sound the atmosphere to the deeper levels.

There are two competing processes that affect the observed CO_2: (1) precipitation of the particles during the night that results in increase of CO_2 in the morning and (2) eddy diffusion of SO_2 in the night that enhances SO_2 above the clouds, forms sulfuric acid above the clouds in the morning and screens CO_2. It looks like both effects balance each other in our morningside observations.

3.2. CO_2 column density at 3.66 and 4.04 μm

Retrievals of HDO and HCl from our observations require a CO_2 spectrum near 3.7 μm, and we chose the $CO^{18}O$ lines observed at $\nu_0 = 2731\ cm^{-1}$ (Fig. 1, upper panel). Thermal emission of the atmospheric foreground is ∼30% of the observed brightness of Venus. This emission is spectrally uniform near 2731 cm^{-1} and may be caused by the atmospheric aerosol. We subtract this emission from the spectra of Venus. The P32e and P33e lines are stronger than the other $CO^{18}O$ lines in the spectrum and not contaminated by the solar and telluric lines. This has been checked using both ATMOS and ACE solar spectra (Hase et al., 2010) and the HITRAN database. The $^{18}O/^{16}O$ ratio on Venus is equal to the terrestrial value, and a code to retrieve CO_2 column densities is similar to that at 2.25 μm. The results are given in Fig. 2.

This figure shows that CO_2 at 3.66 μm is smaller than that at 2.25 μm by a factor of ∼4, and both observations were almost simultaneous. We suggest the following explanation to this difference. Our calibration by the infrared standard stars results in Venus reflectivity at low latitudes ±30° $\rho = \pi I/I_0 / \cos z = 0.7$ at 2.25 μm and 0.028 at 3.66 μm. Here I_0 is the solar irradiance taken from Pierce and Allen (1977). The high reflectivity at 2.25 μm means that the single scattering albedo is ∼1, multiple scattering

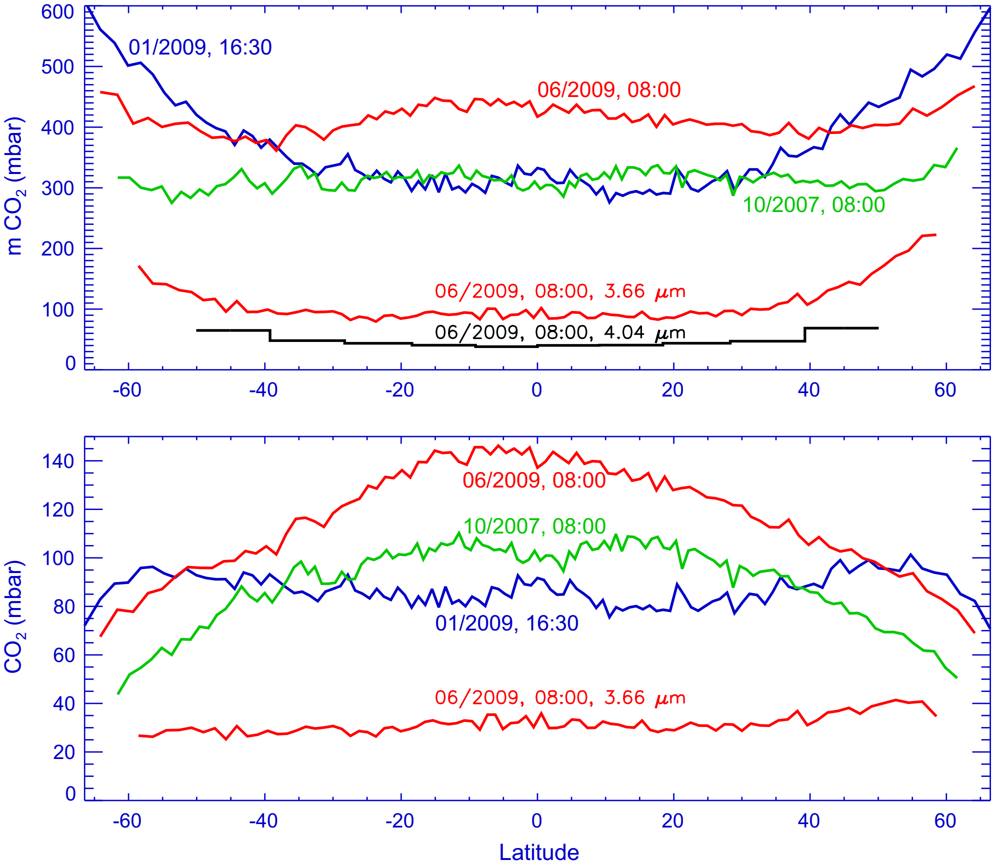

Fig. 2. Retrieved CO_2 column densities (lower panel) and their products by airmass (upper panel) for three observing sessions at 2.25 μm and one observation at 3.66 μm and 4.04 μm. Airmass increases from ~3 at the low latitudes to ~7 near ±60°.

dominates in the clouds, and the effective reflection level may be estimated as $m\tau(1-g)\approx 1$ (van de Hulst, 1980). Here g is the scattering asymmetry factor which is equal to ~0.75 in Venus clouds (Moroz, 1983). The reflectivity is very low at 3.66 μm because of a strong absorption by sulfuric acid, the single scattering albedo is low as well, multiple scattering may be neglected, and the effective reflection level is at $m\tau\approx 1$. The difference in τ is a factor of 4, similar to that observed for CO_2. This also favors a uniform mixing of the aerosol in the atmosphere.

CO_2 column densities are also extracted from our spectra at 2476 cm^{-1} (4.04 μm) observed in June 2009 to measure SO_2 on Venus. The derived mCO_2 values are shown in Fig. 2. They are even smaller than those at 3.66 μm by a factor of 2. Thermal radiation becomes significant at 4.04 μm, and absorption of thermal radiation is partly compensated by thermal emission. This helps to explain the low CO_2 column densities at 4.04 μm.

4. CO mixing ratio

A code to retrieve a species mixing ratio from an equivalent width of its absorption line is similar to the code for the CO_2 lines described in Section 3.1. That is, the equivalent width is calculated by integration of the Voigt line shape from 90 km down to the effective reflection level, and the species mixing ratio is a parameter to fit the observed equivalent width. Temperature and pressures are taken from VIRA, the CO line strengths for various T from HITRAN 2008, and the CO line broadening in CO_2 from Sung and Varanasi (2005).

The CO P21 line was applied to retrieve the CO mixing ratio from the observations in October 2007 (Paper I). Later we chose the CO lines R20 4324.410 cm^{-1} and R21 4326.681 cm^{-1} (Fig. 3) that are not blended by the telluric lines at both signs of the Doppler shift. However, all CO lines are contaminated by the solar CO lines, and equivalent widths of the solar lines should be subtracted from the measured equivalent widths in our spectra. That was not made in Paper I, and the CO data were overestimated there by ~20 ppm. The corrected CO mixing ratios from the observation in October 2007 and the results for January 2009 and June 2009 are shown in Fig. 4.

The mean CO mixing ratios and their variations given as standard deviations are 51 ± 7 ppm and 52 ± 5 ppm in the morning and 40 ± 4 ppm in the afternoon (Fig. 4). These standard deviations are not random errors of the mixing ratios that are of a few percent. However, we do not rule out systematic errors up to 15%. The derived mixing ratios refer to the half CO_2 level, that is, to ~50 mbar or 68 km.

Connes et al. (1968) retrieved the CO mixing ratio of 45 ± 10 ppm; Young (1972) reanalyzed their spectra and got 51 ppm. Observations of the CO (1-0) band at 4.7 μm by the VIRTIS-M spectrograph at Venus Express (Irwin et al., 2008) reveal no significant variations of the CO mixing ratio on the Venus nightside at the low and middle latitudes with a mean value of 40 ± 10 ppm. All these data refer to 65–70 km. Three CO profiles from the SOIR occultations (Vandaele et al., 2008) end near 67 km and give 15, 26, and 40 ppm at 67–70 km. The SOIR results were measured at high latitudes 73–84°N. Our results agree with the previous CO values obtained by infrared spectroscopy.

CO is measured in the millimeter and submillimeter ranges since its detection in these ranges by Kakar et al. (1976). The CO rotational lines 1 → 0, 2 → 1, and 3 → 2 at 2.6, 1.3, and 0.8 mm, respectively,

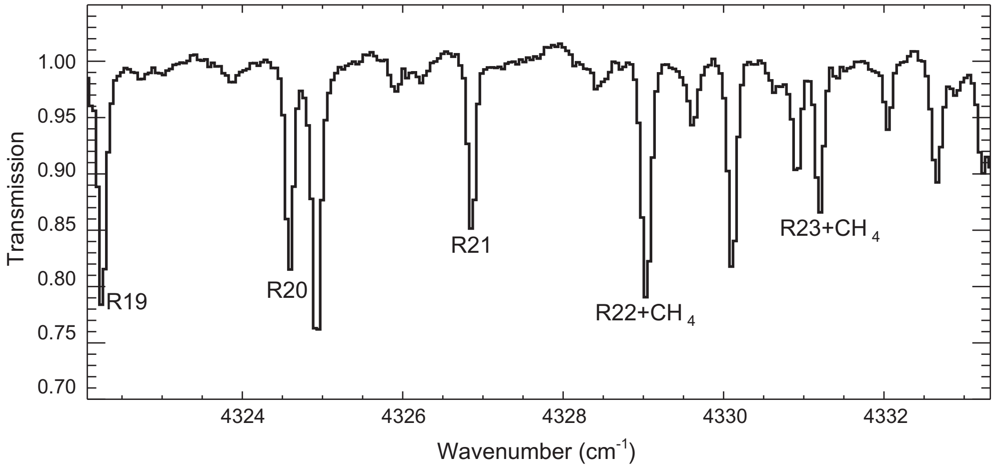

Fig. 3. Spectrum of the CO (2-0) lines observed in January 2009. The CO and solar lines are Doppler-shifted by 0.183 cm^{-1}. Other features are telluric H_2O and CH_4 and solar lines.

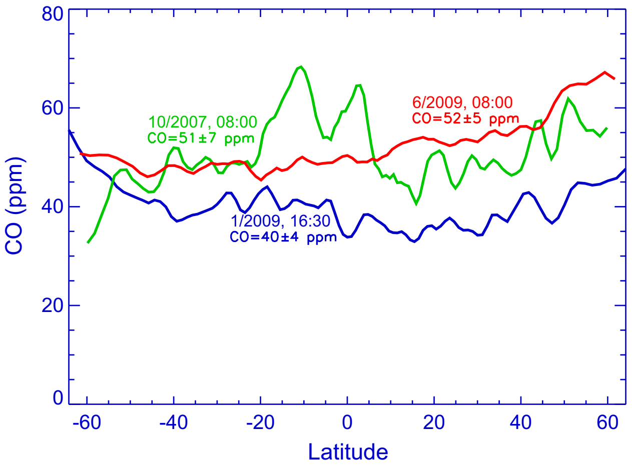

Fig. 4. Latitudinal variations of the CO mixing ratio in two morningside and one afternoon observations.

are used. The signal is transformed to radio frequencies by the heterodyne technique, and this makes it possible to reach extremely high spectral resolving power ~10^7. Simultaneous measurements of the optically thick CO and optically thin ^{13}CO line profiles result in retrieval of both CO and *T* profiles in the altitude range of 75–105 km. Observations at different phases of Venus and/or with low spatial resolution (e.g. five parts of the Venus disk in Clancy et al. (2008)) revealed a morningside CO bulge in the mesosphere (70–120 km). The spatial resolution was significantly improved to 2.8 arcsec using the interferometric technique at two phases of Venus and gave a three-dimensional distribution of CO (Gurwell et al., 1995). The observed CO bulge is maximal at 100 km and extends from 18 h to 8 h in local time and at ±60° in latitude. The bulge is not so prominent at 90 km. The dayside CO mixing ratio is ~60 ppm at 80 km and ~600 ppm at 100 km (Clancy et al., 2008).

The mean values in our observations (Fig. 4) are similar in the morningside sessions, though the curves look different with two significant peaks at the low latitudes and higher variability in the observations in October 2007. The difference between the morning and afternoon mixing ratios exceeds small-scale variations of CO and indicates that some residual of the mesospheric morningside CO bulge extends to the cloud tops.

A weak increase of CO from low latitudes to the limbs is seen at best in the afternoon curve. The effective altitude is raising at large airmass near the limb, and this increase reflects the growth of the CO mixing ratio with height.

CO is formed by photolysis of CO_2 above the clouds. According to the chemical kinetic model (Krasnopolsky, 2007), the downward flux of CO is partially consumed in the reaction with SO_3 at 30–40 km and then in the reactions with sulfur in the lowest 10 km. Observations by the Venera 12 (Gelman et al., 1979) and Pioneer Venus (Oyama et al., 1980) gas chromatographs, spectroscopy of the nightside from ground-based observatories (Pollack et al., 1993; Bezard and de Bergh, 2007) and Venus Express (Marcq et al., 2008) confirm the decreasing CO mixing ratio to 20–30 ppm at 36 km with a further decrease to the surface.

5. HF mixing ratio

Bulges of light species in the Venus upper atmosphere were discovered by the neutral and ion mass spectrometers at the Pioneer Venus orbiter (Niemann et al., 1980; Brinton et al., 1980). The bulges extend into the mesosphere and even to the cloud tops, as we discussed in the previous section.

HF is another light species with a long chemical lifetime. It is even lighter than CO with masses of 19 and 28, respectively. It is not clear whether HF forms a bulge or not. HF was detected for the first time by Connes et al. (1967) with a mixing ratio of 5 ± 2 ppb at the cloud tops. Bjoraker et al. (1992) observed 6.5 ± 0.3 ppb at 72 km, and SOIR at Venus Express measured three vertical profiles of HF at 67–94 km (Vandaele et al., 2008). The profiles vary within 1–7 ppb with a mean value of 3.3 ppb at 67–70 km. All three profiles were measured at subpolar latitudes 70–88°N. The HF abundance is too low to be measured by mass spectrometers, and the existing observations are insufficient to make any conclusion about the HF bulge.

We observed HF at 08:00 in October 2007 and at 16:30 in January 2009. A spectrum measured near the equator in January 2009 is shown in Fig. 5. Mixing ratios of HF are retrieved from the measured line equivalent widths as described for CO in Section 4. The HF line broadening by CO_2 is taken from Shaw and Lovell (1969). The broadening exponent is unknown for HF in CO_2, and the value *n* = 0.55 from HITRAN for HF in the air is adopted. Latitudinal variations of the HF mixing ratio in the morning and in the afternoon are shown in Fig. 6.

The mean HF mixing ratios and their variations given as standard deviations demonstrate perfect similarity in both observations. Therefore, contrary to CO, there is no variation of the HF

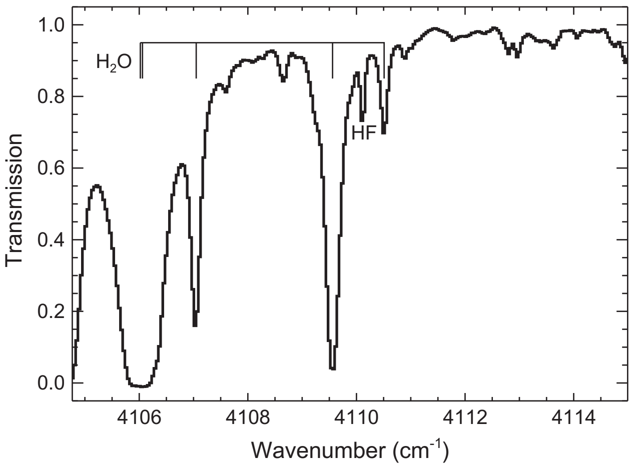

Fig. 5. Spectrum observed in January 2009 near the equator to measure the HF (1-0) R3 line at 4109.94 cm^{-1}. The line is Doppler-shifted by 0.174 cm^{-1}.

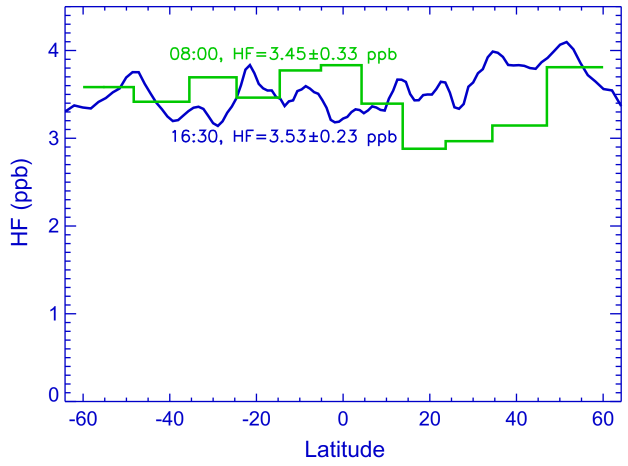

Fig. 6. Latitudinal variations of the HF mixing ratio in the morning and in the afternoon from the observations in October 2007 and January 2009, respectively.

mixing ratio with local time. This does not favor a HF bulge but generally does not rule it out higher in the atmosphere than 68 km in our observations. Probably, the bulges are more prominent if a species is formed in the upper atmosphere and flows down to the middle and lower atmosphere. This is the case of CO but not HF. However, the He bulge has been observed (Niemann et al., 1980), and both He and HF are long living species on Venus. Therefore the problem needs further study.

The measured HF mixing ratio of 3.5 ppb is in reasonable agreement with the previous observations at the cloud tops. It may be also compared with that derived from the high-resolution spectrum of the nightside at 2.3 μm (Bezard et al., 1990) which gives 5 ± 2 ppb in the lower atmosphere at 30–40 km (Bezard and de Bergh, 2007). Retrievals of the lower atmospheric composition from the VIRTIS-H spectra observed at Venus Express (Marcq et al., 2008) do not involve HF.

There are no limb brightening or darkening in the HF mixing ratio in our observations. This means that it is rather constant at 65–75 km. The HF measurements at the cloud tops agree with that in the lower atmosphere, and the HF mixing ratio does not vary with height.

If HF is uniformly mixed in the atmosphere, then both vertical and horizontal winds do not change its mixing ratio, and the observed place-to-place variations in Fig. 6 may be caused by changes in the effective reflection level that are not perfectly compensated in our analysis.

6. HCl mixing ratio

HCl was detected on Venus for the first time by Connes et al. (1967) with a mixing ratio of 0.6 ± 0.12 ppm; Young (1972) retrieved 0.42 ± 0.07 ppm from their spectra. Absorption lines of HCl were observed in the high (Bezard et al., 1990; Bezard and de Bergh, 2007) and medium (Pollack et al., 1993) resolution spectra of thermal emission from the Venus nightside at 1.7 μm. The measured HCl mixing ratio is 0.5 ± 0.15 ppm at 15–30 km.

Iwagami et al. (2008) observed spectra of the nightside thermal emission at 1.74 μm in 1999 with resolving power of 900; the retrieved HCl mixing ratio is 0.4 ± 0.05 ppm at 12–24 km. They also observed HCl on the dayside in 2007 using CSHELL and derived the mixing ratio of 0.74 ± 0.06 ppm at the cloud tops. Difference between the two values significantly exceeds their claimed uncertainties, and the authors conclude that there is a source of HCl in or above the clouds.

All above measurements of HCl were made using lines of the (2-0) band at 1.76 μm. The SOIR occultations at Venus Express (Vandaele et al., 2008) at the R0–R4 lines of the (1-0) band at 3.44 μm result in vertical profiles of the HCl mixing ratio at 72–106 km. The mean mixing ratio in three published profiles is equal to 0.1, 0.15, 0.06, and 0.13 ppm at 72, 80, 88, and above 97 km, respectively. The published profiles refer to subpolar latitudes 73–84°N and are rather similar with the minimum at 88 km. Therefore there is a significant difference between the existing measurements of HCl at the cloud tops.

We observed the R5 lines of the (2-0) band of HCl in January 2009. A spectrum measured near the equator is shown in Fig. 7, and the lines of both isotopes $H^{35}Cl$ and $H^{37}Cl$ are seen in the spectrum. We have not found in the literature a high-resolution solar spectrum for this range observed outside the atmosphere. A solar spectrum observed at the Kitt Peak National Observatory with resolution of 0.004 cm^{-1} is taken from http://bass2000.obspm.fr/solar_spect.php, converted from wavelengths in the air to wavenumbers in vacuum, and shown in the upper panel of Fig. 7. Wavenumbers in the two spectra coincide for the telluric lines and are different for the solar lines because of the Doppler shift. We calculated a synthetic spectrum of the telluric absorption that also helps to distinguish between the solar and telluric lines.

The rest and Doppler-shifted positions of the HCl lines are shown in the figure. We conclude that the line coinciding with the rest $H^{35}Cl$ line is solar. Both $H^{35}Cl$ line and the solar line are Doppler-shifted and remain coinciding in our observation. The lines near the $H^{37}Cl$ line are from telluric CH_4 and are blended in our observation. Equivalent widths of the $H^{35}Cl$ lines were corrected for the solar line and used to derive the HCl mixing ratio at 68 km using the technique described in Section 4. The mean HCl mixing ratio is 0.47 ± 0.11 ppm (Fig. 8), and its standard deviation reflects both variations of HCl and random errors. The HCl line broadening by CO_2 is taken from Toth and Darnton (1974). The broadening exponent is unknown, and the value for air from HITRAN $n = 0.35$ is adopted in our calculations.

Our observation of HCl in June 2009 was made using the P8 lines of the (1-0) band. The ATMOS and ACE solar spectra and a synthetic spectrum of the telluric absorption show that the lines are spectrally clean. The line strengths are near the end of the linear part of the curve of growth for HCl ≈ 0.5 ppm, that is, near the optimum for careful retrieval. However, both the solar flux and Venus' albedo are low in this range, and the observation required much longer exposure than for the (2-0) lines. The measured spectra were corrected for the sky thermal foreground that was ~30% of the total signal. A spectrum observed near the equator is shown

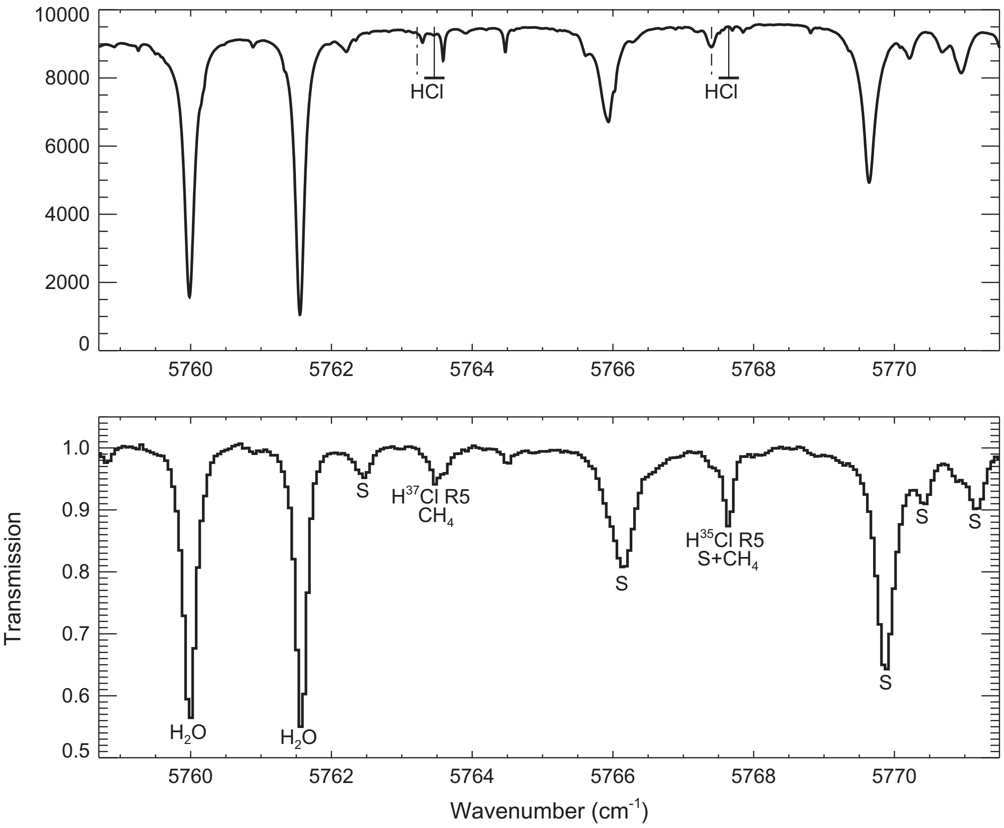

Fig. 7. Lower panel: spectrum near the (2-0) R5 lines of $H^{37}Cl$ and $H^{35}Cl$ observed at the equator in January 2009. Other features are telluric H_2O and CH_4 and solar lines. The HCl and solar lines are Doppler-shifted by 0.244 cm^{-1}. Upper panel: solar spectrum measured at the Kitt Peak Observatory. Wavenumbers of solar lines are different in the two spectra because of the Doppler shift. Unshifted and shifted positions of the HCl lines are shown; each horizontal bar indicates two CSHELL resolution elements.

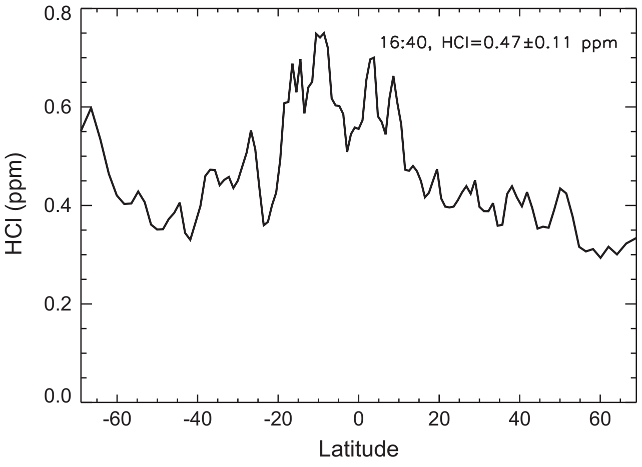

Fig. 8. Latitudinal variations of the HCl mixing ratio at 16:40 retrieved from the R5 (2-0) line of $H^{35}Cl$. The standard deviation reflects both true variations and random errors.

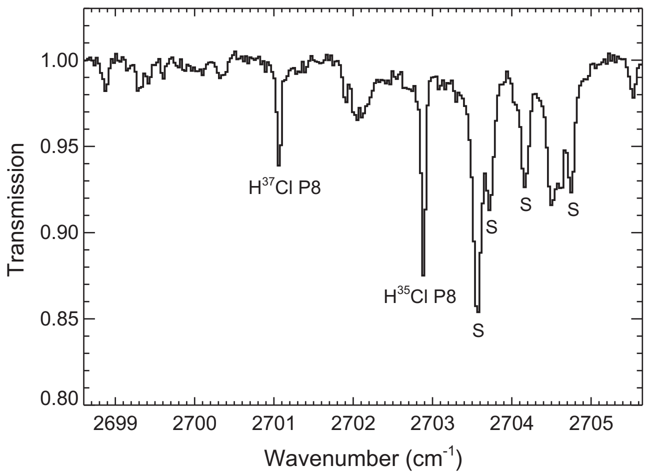

Fig. 9. Spectrum near the (1-0) P8 lines of $H^{37}Cl$ and $H^{35}Cl$ observed in June 2009. Other features are telluric H_2O and CH_4 and solar lines. Some strong solar lines are marked S. The wavenumber scale is Doppler-shifted by -0.122 cm^{-1}.

in Fig. 9. The HCl mixing ratios were extracted using our technique with the CO_2 column densities (Fig. 2) from the spectra at 2731 cm^{-1} (Fig. 1). The mean HCl mixing ratio is 0.37 ± 0.03 ppm and 0.46 ± 0.05 ppm retrieved from the $H^{35}Cl$ and $H^{37}Cl$ lines, respectively (Fig. 10). The difference exceeds the standard deviations and indicates either an enriched ^{37}Cl on Venus or a systematic error, and the latter looks more probable.

Actually the $H^{35}Cl$ line is stronger than the $H^{37}Cl$ by a factor of 3. The broadening exponent is unknown for HCl in CO_2, and the value for the air from HITRAN $n = 0.13$ adopted by us is very low (usually $n \approx 0.75$). That may be reasons for the systematic error while the significant difference in $^{37}Cl/^{35}Cl$ on Venus from the terrestrial value is not expected.

The weighted mean mixing ratio of HCl is 0.40 ± 0.03 ppm from our observations. It refers to a level of $0.5CO_2 = 15$ mbar (Fig. 2), that is, 74 km according to VIRA. There are no limb brightening or darkening in the curves in Fig. 10, and this favors a constant HCl mixing ratio within ~10 km above the cloud tops.

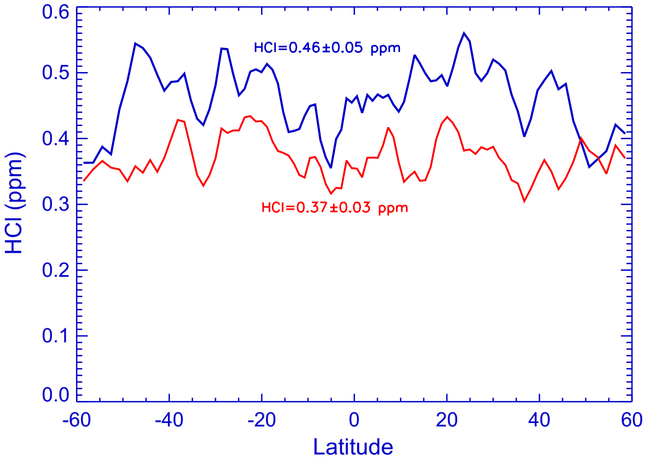

Fig. 10. HCl mixing ratios at 74 km retrieved from the $H^{37}Cl$ (blue) and $H^{35}Cl$ (red) lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The obtained HCl mixing ratio agrees with that from Young (1972) at the cloud tops and the values for the lower atmosphere from Bezard et al. (1990), Pollack et al. (1993), Bezard and de Bergh (2007) and Iwagami et al. (2008). This implies a uniformly mixed HCl from the surface to the cloud tops that is supported by the photochemical model by Mills (1998) at 58–112 km and the chemical kinetic model by Krasnopolsky (2007) at 0–47 km. The high value for HCl at the cloud tops in Iwagami et al. (2008) may be caused by a contamination from the solar and telluric lines.

7. Conclusions

We have observed and analyzed CO_2 and three species (CO, HF, and HCl) discovered four decades ago by Connes et al. (1967, 1968) in the first high-resolution spectra of Venus. The major difference is that now we may apply spatially-resolved spectroscopy to study latitudinal variations of these species, and that has been made in the latitude range of ±60°. Combining morningside and afternoon observations, it is possible to estimate diurnal variations of the species. Furthermore, more accurate spectroscopic data and properties of Venus' atmosphere are currently available and may be used to improve our analysis. More data on the atmosphere of Venus may be involved in comparison with the retrieved mixing ratios.

The observations of the CO_2 lines at 2.25 μm reveal variations of the cloud aerosol density and scale height near 65 km: the aerosol is denser by 25% in October 2007 than in June 2009, and its scale height is smaller in January 2009 than in the two other observations.

Both reflectivity of Venus and the effective CO_2 column densities are smaller at 3.66 μm than those at 2.25 μm: the former by a factor of 25, the latter by a factor of 4. This correlates with the transition from the almost conservative multiple scattering at 2.25 μm to single scattering in the almost black aerosol at 3.66 μm because of strong absorption by sulfuric acid. This transition is described by a factor of $(1-g)^{-1} = 4$, where $g = 0.75$ is the scattering asymmetry factor for Venus' clouds.

The observed CO mixing ratio is 52 ± 4 ppm near 08:00 and 40 ± 4 ppm near 16:30 at 68 km. The latter is probably the mean dayside value while the former reflects extension of the CO morningside bulge to the cloud tops. The observed weak limb brightening in CO indicates an increase of the CO mixing ratio with altitude.

HF is constant at 3.5 ± 0.2 ppb at 68 km in both morningside and afternoon observations and in the observed latitude range ±60°. Therefore our observations do not favor a bulge of HF, though HF is lighter than CO. Probably a source in the upper atmosphere facilitates the bulge formation. This source exists for CO (photolysis of CO_2) and is lacking for HF. However, the bulges may form even without this source, e.g., the He bulge.

The recent measurements of HCl near 70 km are controversial (0.1 and 0.74 ppm) and require either a strong source or a strong sink of HCl in the clouds. The HCl lines of the (2-0) band are blended by the solar and telluric lines. Therefore we observed the P8 lines of the (1-0) band at 3.44 μm. These lines are spectrally clean and result in the HCl mixing ratio of 0.40 ± 0.03 ppm at 74 km. HCl does not vary with latitude within ±60°. Our value agrees with that of Young (1972) and supports a uniformly mixed HCl throughout the Venus atmosphere.

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