

LETTERS

A warm layer in Venus' cryosphere and high-altitude measurements of HF, HCl, H₂O and HDO

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Venus has thick clouds of H₂SO₄ aerosol particles extending from altitudes of 40 to 60 km. The 60–100 km region (the mesosphere) is a transition region between the 4 day retrograde superrotation at the top of the thick clouds and the solar–antisolar circulation in the thermosphere (above 100 km), which has upwelling over the subsolar point and transport to the nightside^{1,2}. The mesosphere has a light haze of variable optical thickness, with CO, SO₂, HCl, HF, H₂O and HDO as the most important minor gaseous constituents, but the vertical distribution of the haze and molecules is poorly known because previous descent probes began their measurements at or below 60 km. Here we report the detection of an extensive layer of warm air at altitudes 90–120 km on the night side that we interpret as the result of adiabatic heating during air subsidence. Such a strong temperature inversion was not expected, because the night side of Venus was otherwise so cold that it was named the ‘cryosphere’ above 100 km. We also measured the mesospheric distributions of HF, HCl, H₂O and HDO. HCl is less abundant than reported 40 years ago³. HDO/H₂O is enhanced by a factor of ~2.5 with respect to the lower atmosphere, and there is a general depletion of H₂O around 80–90 km for which we have no explanation.

The use of solar (at the terminator: the circle on the planet that separates the day side from the night side) and stellar occultation technique (at night), applied for the first time to the atmosphere of Venus with the SPICAV/SOIR spectrometers on board the Venus Express spacecraft, allows us to measure the atmospheric transmission and to derive information about the vertical structure and composition of the 60–140 km region. In this region, many processes (transport, chemistry, temperature, aerosols condensation and evaporation) govern the three-dimensional distribution of haze and chemical species. In the ultraviolet range (110–310 nm) of the SPICAV ultraviolet spectrometer (a copy of the SPICAM ultraviolet instrument in orbit around Mars⁴), the most important absorbers are CO₂ (the main Venus atmospheric constituent) at $\lambda < 200$ nm, and aerosol particles of the haze layer at all wavelengths. The CO₂ local density and temperature profiles are derived by assuming that the atmosphere is in hydrostatic equilibrium⁵ (Supplementary Information).

On Fig. 1 are represented the temperature profiles obtained during six stellar occultations performed on the night side. They are compared to previous and scarce measurements^{6–9}. All our new profiles show a large temperature excess (30–70 K) with respect to previous measurements, peaked around 100 km. The altitude range 100–150 km has largely been unexplored up to now—the upper limit

for infrared soundings and radio occultation is ~100 km, descent probes have so far measured below this range, and drag measurements are made above 150 km. Occultation measurements can probe this region efficiently, allowing the discovery of this hot atmospheric layer. Orbits 95, 96 and 98 have similar profiles, while orbits 102, 103 and 104 have the same kind of profiles, but with an even higher maximum temperature. These three orbits are much closer to the anti-solar point (solar zenith angle, SZA = 167–170°).

We interpret this newly found temperature peak to be caused by adiabatic (or diabatic) heating during air subsidence near the anti-solar point, as the end result of the solar–antisolar circulation pattern suspected to exist in the thermosphere (100–200 km) from the day side to the night side. Such heating was not well predicted by current circulation models, although there was evidence of day-to-night transport and downward vertical transport on the night side: the emission of NO ultraviolet delta and gamma bands already observed by Pioneer Venus^{10,11}, and O₂ emission at 1.27 μ m discovered from the ground¹² (also well detected with VIRTIS/VEX¹³). These emissions occur when O and N atoms (produced by solar extreme-ultraviolet photo-dissociation of N₂ and CO₂ on the day side at 100–120 km) recombine in the night side. However, modelling of NO ultraviolet emission^{11,14} described N and O atoms as being transported vertically downwards through the CO₂ background gas by eddy diffusion (turbulence).

In such a description, the CO₂ background gas does not move vertically, and therefore experiences no adiabatic heating. Our observations indicate rather that N and O atoms are advected downwards with the CO₂ background gas during its descent. Such a vertical atmospheric motion is an essential ingredient of the solar–antisolar circulation pattern, which may influence the behaviour of the whole mesosphere, because it implies a compensating upwelling on the day side. The descent velocity may be estimated, given that at temperature $T = 165$ K the night-time infrared cooling rate is about 100 K per day (ref. 2). Assuming a T^4 dependence, it would amount to 377 K per day for a temperature of 230 K as measured here near the anti-solar point. This cooling rate can be compensated by an equal adiabatic heating rate, corresponding to a descent velocity $V = 0.43$ m s⁻¹, using the relation $dT/dt = -\Gamma V$ where t is time and Γ is the adiabatic lapse rate (about 10 K km⁻¹; ref. 15). The negative temperature gradient in the layer at 100–120 km is on average equal to -5 K km⁻¹ for orbit profiles 102 to 104 and locally reaches values near the adiabatic lapse rate. This suggests that the layer at 100–120 km is dynamically nearly unstable and that turbulence may occur, inducing a downward heat flux by

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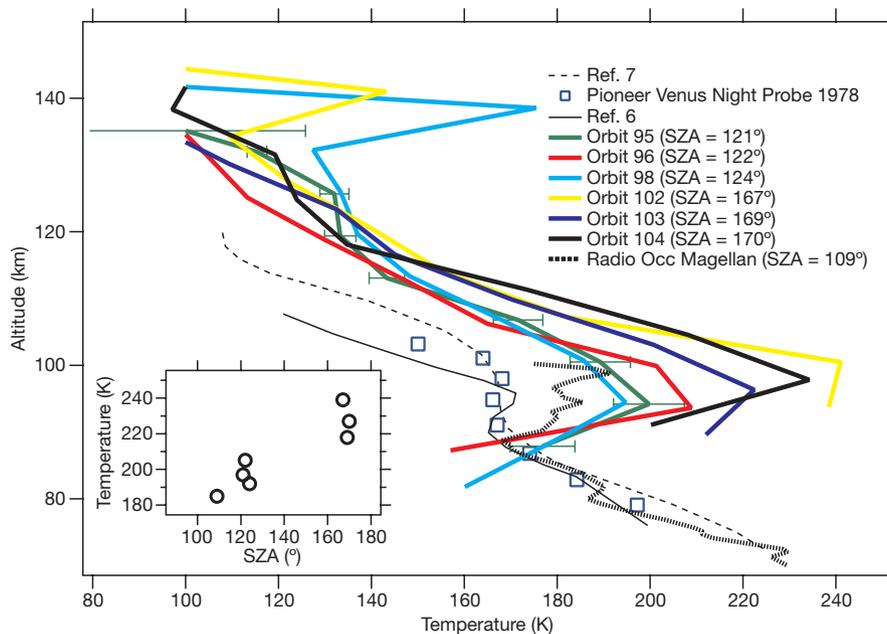


Figure 1 | Night-side temperature of Venus atmosphere. The mesopause may be defined at 90 km of altitude, separating the mesosphere (<90 km) from the lower thermosphere (>90 km). Solid thick curves, obtained by stellar occultations on the night side from Venus Express (this work), are compared to previous measurements. The blue squares were obtained during the descent of the Pioneer Venus night-side probe. The thin solid line shows sub-millimetre observations from a ground-based radio-telescope, Venus disk integrated⁶. The dashed line shows millimetre observations from a ground-based radio-telescope, Venus disk integrated⁷. The thick dotted line was obtained from a radio-occultation of the Magellan orbiter⁹, at a SZA

of 109°. This single measurement shows an increase of temperature at altitudes above 85 km, similar to the ones seen in this work, but less pronounced. The SPICAV error bars (1σ) are indicated for orbit 95 (green) and are typical of the errors for the other curves. The two groups of measurements were taken at latitude 39° N (local time ~21:00 h, SZA = 121–124°) for orbits 95, 96, 98 and latitude 4° S (local time ~23:20 h, SZA = 167–170°) for orbits 103, 103 and 104. The orbit is 24 h long. There is a clear pattern for the value of the maximum temperature (90–100 km), increasing with the SZA, as emphasized in the bottom left plot (the point at SZA = 109° is from Magellan).

mixing of potential temperature and a reinforcement of the peak temperature.

This is the first time that a temperature inversion is so clearly identified at this altitude in the night-side atmosphere of Venus. However, there is a hint of temperature inversion in previous data at their maximum altitude soundings: a 2–4 K increase from 95 to 100 km in infrared spectra⁸, and a 10 K increase from 90 to 100 km in the radio-occultation profile of Magellan⁹ taken at a SZA of 109°. We note that, in our profiles, the higher (the nearer to the anti-solar point) is the SZA, the higher is the temperature maximum, this trend being confirmed on the low side of the SZA by Magellan (which has an excellent vertical resolution and sampling). Whether our new hot profiles are sporadic and patchy, or are permanent and large-scale features (having escaped detection before) will be clarified by future Venus Express measurements.

Hydrogen-bearing molecules (HCl, HF, H₂O and HDO) are broken by solar ultraviolet in the altitude range 80–120 km, and their abundance in the mesosphere is relevant to the ultimate escape rate of H, and possible evolution of the Venus atmosphere. HCl and HF were discovered in 1967 (ref. 3). More recently, the abundance of HDO (ref. 16) and H₂O (ref. 17) above cloud top were found to experience large time variations (by a factor of 30), even when the measurements were averaged over the whole disk of Venus, with no explanation as yet. Almost nothing is known about the vertical profile of these species, although it is essential for modelling of H escape. A new compact high-spectral-resolution infrared instrument, called Solar Occultation in the InfraRed (SOIR)¹⁸ was implemented on Venus Express as an extension of SPICAV, to measure the vertical distribution of hydrogen-bearing species in the range 60–110 km by the technique of solar occultation at terminator (see the Supplementary Information). SOIR is a new type of spectrometer, with an echelle spectrometer associated to an acousto-optical tunable filter for wavelength domain selection, measuring the solar spectrum and the atmospheric transmittance (Fig. 2) in the infrared region

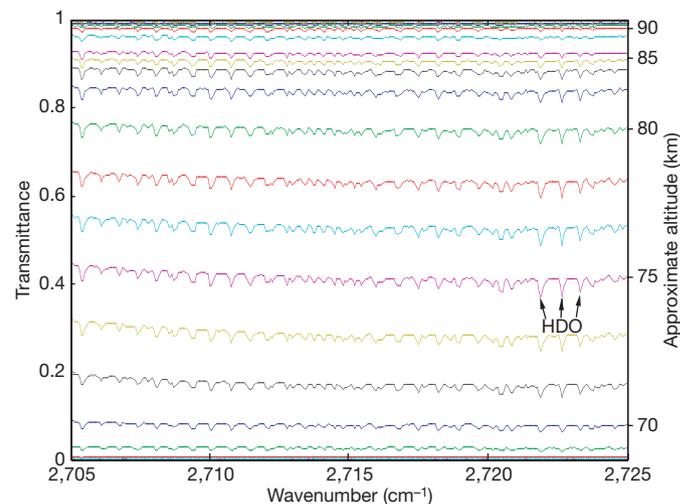


Figure 2 | Typical evolution of atmospheric spectral transmittances through one solar occultation observed by SOIR spectrometer. It is obtained by determining the ratio of the solar spectrum seen through the Venus atmosphere to the unattenuated solar spectrum measured above the atmosphere, at high spectral resolution and a 3 to 6 km altitude sampling. At the beginning of the series, the light path does not cross the atmosphere. No absorption signatures are present and transmittances are equal to unity. As the sun sets, the light path goes deeper and deeper into the atmosphere, and two absorption processes take place: the overall signal decreases owing to extinction by aerosols, and gaseous absorption signatures appear. At the end, the light path crosses the cloud layer located at an altitude around 60 km above the Venus surface (at 6,051.5 km radius) and light is no longer transmitted. This solar occultation was collected on 26 November 2006 during a sunset. The selection of a spectral interval is achieved through the acousto-optical tunable filter, tuned in this case to the 2,703.5–2,727.5 cm⁻¹ spectral range. In this particular range, the main absorption lines are from HDO (a trio of lines indicated by arrows), and other features are from weak CO₂ spectral lines.

(2.2–4.3 μm) at a resolution of 0.15 cm^{-1} . At present, using it, absorption structures of CO_2 , H_2O , HDO , CO , HCl and HF have been observed with certainty.

Retrieval of the vertical distribution of the various species is done by comparing the observed transmittance spectra to a full forward model simulation¹⁹. Some results of this best-fit exercise are shown in Fig. 3 for HF and HCl . The abundance of HF measured below the clouds²⁰ at 0.005 ± 0.002 p.p.m. agrees with other measurements²¹ corresponding to altitudes above 72 km (0.0065 ± 0.0003 p.p.m.). Our SOIR-measured values (0.001 to 0.003 p.p.m. at 75–85 km) are significantly lower (by a factor of 3).

At altitudes between 15 and 30 km, lower than those probed by the SOIR instrument, an HCl mixing ratio of 0.5 ± 0.15 p.p.m. was obtained in 1989 (ref. 20) while a similar value of 0.6 ± 0.12 p.p.m. was found³ in 1967 above the clouds (60 km). The abundances of HCl obtained from the SOIR measurements during the occultations of orbits 136 and 247, shown in Fig. 3a, are slightly different from each other (by a factor of ~ 1.5 at 70–75 km), and are lower than values reported in the literature (factor of 4 to 6): 0.1 ± 0.03 p.p.m. for orbit 136 and 0.17 ± 0.03 p.p.m. for orbit 247, both at 70–75 km. Current models of photochemistry of the atmosphere of Venus above the clouds²² are assuming a value of 1 p.p.m.v. of HCl for this very active component and should be revised accordingly. Another possible explanation of our low values is that the solar occultation probed a high latitude, where thermospheric air depleted in HF and HCl (because of photo-dissociation at high altitude) may be spiralling down the polar vortex, along the descending branch of the Hadley's cell whose up-leg is at the subsolar point (Y. L. Yung & R. T. Clancy, personal communication).

Figure 4a shows retrievals of H_2O and HDO mixing ratios obtained simultaneously with the acousto-optical tunable filter sequence alternating between the H_2O spectral window and the HDO window, and with a window also dedicated to CO_2 retrieval.

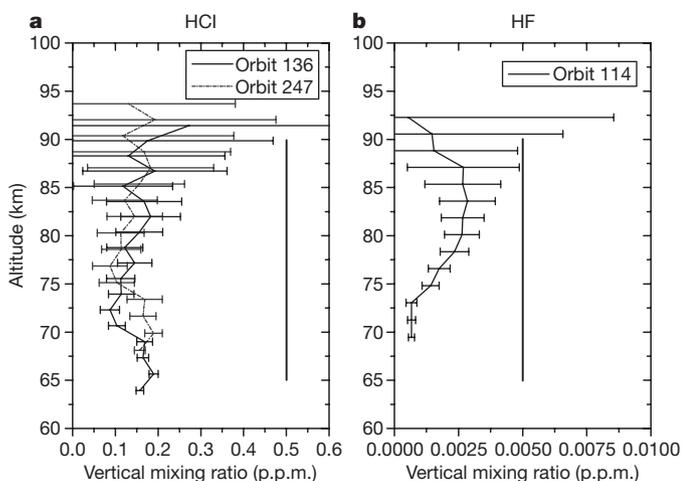


Figure 3 | HF and HCl mixing ratio vertical profiles retrieved from SOIR occultations. The mixing ratios are computed from the density retrievals of HF and HCl , divided by the CO_2 density retrieved from CO_2 absorption lines. The number of the orbit analysed is indicated on each graph. **a**, Two HCl profiles are compared, taken at orbit 136 (4 September 2006) and 247 (24 December 2006). They are somewhat different in the range 70–75 km of altitude, and the mixing ratio seems to increase slightly with altitude in both profiles. Error bars are 1σ . The amount of HCl is much less than is assumed in the photochemistry models (1 p.p.m.), and less than 0.6 ± 0.12 p.p.m. reported above the clouds³, even after revision of this measurement to 0.42 ± 0.07 p.p.m. (ref. 28). The vertical bar represents a constant volume mixing ratio of 0.5 p.p.m., as an average of the two derivations^{3,28} from 1967 observations. **b**, The HF (hydrofluoric acid) volume mixing ratio SOIR profile at orbit 114 (13 August 2006) is somewhat lower by a factor of ~ 3 than a previous measurement corresponding to altitudes above 72 km (vertical bar).

The three profiles were obtained over 18 days, at a high north latitude (80–75°) terminator. H_2O is at 0.3–1 p.p.m.v, an intermediate value within the very large range of 0.1 to 4 p.p.m.v reported from previous measurements by different techniques^{16,17} at various times. At variance, our three vertical profiles show little time variability in this limited sample. There is a marked depletion of H_2O in the range 80–90 km, for which we have no explanation yet, other than noting that this altitude range coincides with the mesospheric minimum temperature and the top of the haze layer. For H_2O , there is no abrupt decreasing at high altitudes (up to 110 km), which would be a sign of local condensation.

The $\text{HDO}/\text{H}_2\text{O}$ ratio profiles (Fig. 4b) are quite similar. At the lower boundary of our measurements (70 km), the $\text{HDO}/\text{H}_2\text{O}$ ratio is ~ 0.1 with an error bar (1σ) exceeding 50%, which encompasses the value of 0.05 measured in the bulk atmosphere at lower altitudes^{20,23–25} (to be compared to the Earth's value of 1/3,000). Although we could have expected a decrease of this ratio with increasing altitude because of preferential condensation of HDO ²⁶, the trend is instead an increase in the $\text{HDO}/\text{H}_2\text{O}$ ratio, up to a value of 0.12, about 2.5 times the bulk atmosphere value. Hence, there is no effective cold trap preventing the photo-dissociation of HDO in the upper atmosphere. The observed bulge of HDO at 90–95 km, above the haze and free from extinction of solar flux, might be due to a lower photo-dissociation rate of HDO (versus H_2O), as has been suggested for Mars from laboratory cross-section measurements²⁷.

Alternatively, it could be a sign that H atoms are escaping to outer space faster than D atoms (because of their larger thermal velocity): D atoms left behind in excess will recombine with OH radicals, generating a downward flow of HDO . If this interpretation is correct, it would be the first indication of this expected differential escape of H versus D, acting at present, that could explain the high D/H ratio in the present atmosphere of Venus. However, while the present 3 cm

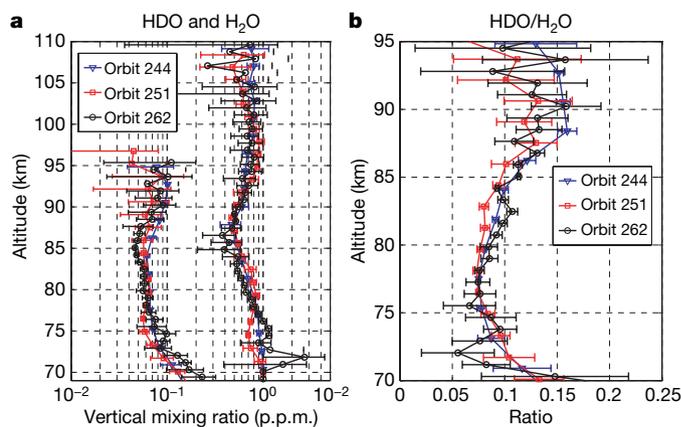


Figure 4 | HDO and H_2O mixing ratio, $\text{HDO}/\text{H}_2\text{O}$ vertical profiles. Both H_2O and HDO were measured simultaneously with SOIR during solar occultation at orbits 244, 251 and 262 between 70 and 110 km respectively at polar latitudes $+85, 83, 73^\circ$ (December 2006 to 8 January 2007). Error bars are 1σ . **a**, HDO slant densities were deduced using absorption structures located around $2,722.5 \text{ cm}^{-1}$ (Fig. 2) and those of H_2O from structures in the $3,832.0\text{--}3,852.0 \text{ cm}^{-1}$ spectral interval. After vertical inversion to obtain local densities, they were divided by the CO_2 density retrieved simultaneously from CO_2 absorption lines to get the volume mixing ratios. The curves above are for HDO (the three curves on the left). The curves of both isotopes show little variability, but there is an unexplained and consistent H_2O depletion around 85 km. **b**, The $\text{HDO}/\text{H}_2\text{O}$ ratio vertical profiles are compared for the three orbits. While this ratio is 1/3,000 in Earth's sea water, Venus is known to be enriched in HDO by a factor of 150, as a result of preferential escape of the lighter isotope $\text{H}^{20,23-25}$. The value of this ratio in the bulk lower atmosphere is measured to be 0.05, while SOIR finds a higher ratio in the whole range 70–95 km. The $\text{HDO}/\text{H}_2\text{O}$ ratio increases with altitude, reaching about 0.12 (a factor of 2.5 above the bulk ratio). For a tentative explanation of this deuterium-super-enriched layer, see text.

equivalent liquid of water and D/H ratio ≈ 0.025 (enrichment 150) would imply a global quantity of water of only 4.5 m depth in the past compared to Earth's 2.8-km-deep ocean (if there were no D escape), a significant escape of D atoms could largely increase this lower limit. The observed presence of HDO in the photo-dissociation region indicates that D atoms must be present in the thermosphere, where they might suffer non-thermal escape mechanisms, as well as H atoms. It is therefore important to quantify the non-thermal escape mechanism of H and D atoms.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

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