



Note

A layer of ozone detected in the nightside upper atmosphere of Venus

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ABSTRACT

To date, ozone has only been identified in the atmospheres of Earth and Mars. This study reports the first detection of ozone in the atmosphere of Venus by the SPICAV ultraviolet instrument onboard the Venus Express spacecraft. Venusian ozone is characterized by a vertically confined and horizontally variable layer residing in the thermosphere at a mean altitude of 100 km, with local concentrations of the order of 10^7 – 10^8 molecules cm^{-3} . The observed ozone concentrations are consistent with values expected for a chlorine-catalyzed destruction scheme, indicating that the key chemical reactions operating in Earth's upper stratosphere may also operate on Venus.

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Ozone is a molecule of fundamental photochemical and exobiological interest. Its absorption continuum in the spectral region between 200 and 300 nm, also known as the Hartley band, is a remarkable spectroscopic ultraviolet (UV) feature as it is both spectrally broad and intense. For this reason, the presence of ozone in a given atmosphere provides efficient filtering of the energetic ultraviolet radiation that reaches the top of the atmosphere. On Earth, 90% of ozone is contained in a so-called stratospheric “ozone layer” located between 15 and 50 km. In fact, ozone is responsible for the very existence of the temperature inversion which defines the Earth's stratosphere, temperature in this altitude range being controlled by solar energy absorbed in the Hartley band. Stratospheric ozone plays a critical role for Earth habitability, reducing ultraviolet to doses acceptable for life development and maintenance. Its formation is controlled by the following reactions:



where (2) is the sole reaction producing ozone, with M denoting a third body required to carry away excess vibrational energy. O_3 production is therefore uniquely dictated by the availability of oxygen molecules, which considering the large reservoir of O_2 on Earth (21% of the atmospheric composition) allows ozone to be sustained at high abundances (3 mm-atmosphere on average, Brasseur and Solomon, 2005). Note that the mm-atmosphere unit measures the vertically integrated column abundance of a given species if brought down to the surface. Ozone abundance is also expressed by the Dobson Unit (DU, one Dobson unit is equivalent to a layer of ozone that would be 10 μm thick under standard terrestrial temperature and pressure); i.e. 2.69×10^{16} molecules cm^{-2} .

The build-up of oxygen on Earth up to the present-day concentration is subsequent to the Great Oxidation Event (GOE) that took place 2.4 billion year ago. The exact causes of the GOE are still not entirely elucidated, but may have involved a

complex interplay between the biological, geophysical and chemical activities of the planet (Farquhar et al., 2000; Catling et al., 2001). Ozone has been identified on Mars since the early 1970s (Barth and Hord, 1971). There, O_2 comes almost uniquely from the photolysis of CO_2 . However, catalytic cycles driven by HO_x radicals (the sum of all hydrogen oxides), efficiently convert O_2 back to CO_2 , limiting O_2 to a minor fraction (0.1%) of the atmospheric inventory. Ozone abundance is consequently low on Mars (<10 μm -atmosphere or <1 DU), typically 300 times less than on the Earth. In spite of its scarcity, martian ozone is a key tracer of the photochemistry that regulates the composition of Mars atmosphere. Through its reaction with HO_x radicals, it appears closely tied to the photochemistry of water and exhibits a strong temporal and spatial anti-correlation with gaseous H_2O , as evidenced by SPICAM onboard Mars Express (Perrier et al., 2006), consistently with model predictions (Lefèvre et al., 2004).

On Venus, the presence of the thick sulfuric acid clouds makes it particularly difficult to probe the atmosphere below 60 km, except in a few infrared windows (Allen and Crawford, 1984). Above the clouds however, ozone was until now not detected despite a total atmospheric density similar to that of the Earth's stratosphere, which suggests it is significantly less abundant than on Earth. The detection that is reported here was made with the Spectroscopy for Investigation of Characteristics of the Atmosphere of Venus (SPICAV) instrument. SPICAV is a remote-sensing spectrometer covering three distinct spectral regions from ultraviolet to mid-infrared that is used to probe the atmosphere above the clouds. It has orbited around Venus onboard the Venus Express spacecraft (Bertaux et al., 2007) since April 2006 (Svedhem et al., 2007). The ultraviolet part of the SPICAV suite probes the 110–320 nm range with a spectral resolution of 1.5 nm. Here, resolution is defined as the full width at half maximum of the spectrometer point spread function. The instrument is sensitive to a large variety of source brightness, ranging from faint stars to the bright Sun. The present work is based on the results of stellar occultations which have been discussed in the case of Mars with SPICAM (Bertaux et al., 2006; Montmessin et al., 2006; Lebonnois et al., 2006), and which have already been presented for Venus (Bertaux et al., 2007). Stellar occultation allows one to infer vertical profiles of aerosols and CO_2 density (the main atmospheric constituent) between 80 and 140 km, a region covering the upper mesosphere and the lower

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thermosphere (Bertaux et al., 2007). Our observations were performed on the night-side of Venus. Several attempts were made on the sunlit hemisphere, but the stellar signal could not be correctly isolated from the bright foreground of the limb due to solar scattering by aerosols.

A detailed inspection of the complete SPICAV dataset allowed to visually identify ozone UV absorption from a stellar occultation sequence during orbit #348 at an altitude of 103 km (Fig. 1). The ozone signature emerges as a moderate, yet distinct reduction of the atmospheric transmission between 220 and 280 nm, with a maximum around 250 nm, consistent with the Hartley band structure. In this spectrum, ozone absorbs 4% of the stellar signal at the band center (Fig. 1D), produced by a slant number density of 8.2×10^{15} molecules of ozone cm^{-2} (~ 0.3 DU) along the line of sight. A factor of $\sim 1/50$ must be applied to convert tangentially integrated densities to vertically integrated densities.

A positive ozone identification is established when the sum of squared residuals in the 220–280 nm range is decreased by a factor of two when the ozone Hartley band is included in the retrieval, yielding a $>5 - \sigma$ confidence level. Instrument signal-to-noise ratio (SNR) is evaluated independently for each occultation sequence by consideration of the intrinsic variability of the ~ 1000 spectra of the star recorded before the occultation by the atmosphere and by the planet. For each spectral element (i.e. pixel), a robust estimator of the mean M_s and of the variance V_s of the signal is obtained that allows to subsequently infer the instrumental gain G (defined as $M_s = GV_s$) with a linear fit of the M_s vs. V_s scatter plot. SPICAV SNR for each pixel is given by $M_s/\sqrt{GV_s}$; yielding an in-flight verified value of $\text{SNR}/\text{pixel} > 50$ for a bright UV star (e.g. ξ CEN), confirming the theoretical estimations made by Korabely et al. (2001) for SPICAV-concept instruments. Sources of noise subsequent to CCD

read-out and CCD dark-current have a minor contribution ($<10\%$) to the noise of SPICAV spectra (at least those containing ozone signature), which are essentially dominated by shot-noise. Data errors are then propagated throughout the extraction process of the abundance of the chemical constituents of interest (e.g. ozone). Uncertainties on the end products of the retrieval (ozone column abundances) are eventually given by the square root of the diagonal terms in the free parameter space covariance matrix computed by the Levenberg–Marquardt chi-square minimization algorithm. 29 different orbits bear the unambiguous signature of ozone, out of a total of more than 286.

For orbit #348, an ozone signature at 103 km is not firmly identified in the adjacent spectra recorded 5 km below and 5 km above the detection altitude. This implies that ozone exists as a discrete layer confined within 5–10 km of altitude. This vertical layering is generally verified for the other 28 orbits where ozone has been detected (Fig. 2-left). The ozone layer is even more prominent in the local concentration profiles that are obtained after vertical inversion of the integrated abundance. The conversion from slant-integrated abundances to local concentrations of ozone is performed via standard onion-peeling procedure. On a few orbits, several consecutive spectra exhibit a firm ozone signature: four detections spanning the 92–105 km range are made on orbit #204, resulting in a O_3 local concentration peak of 6×10^7 molecules cm^{-3} at 92 km (Fig. 2-right). Here, the layer is characterized by a factor of two decrease of ozone concentration 5 km below and 5 km above the peak. On average, the retrieved local concentrations range between 10^7 and 10^8 molecules cm^{-3} at a pressure of 1 μbar , yielding 0.1–1 ppmv in mixing ratios.

The theoretical presence of ozone on Venus has been investigated by means of one dimensional photochemistry models (Yung and DeMore, 1982, 1999; Krasnopolsky,

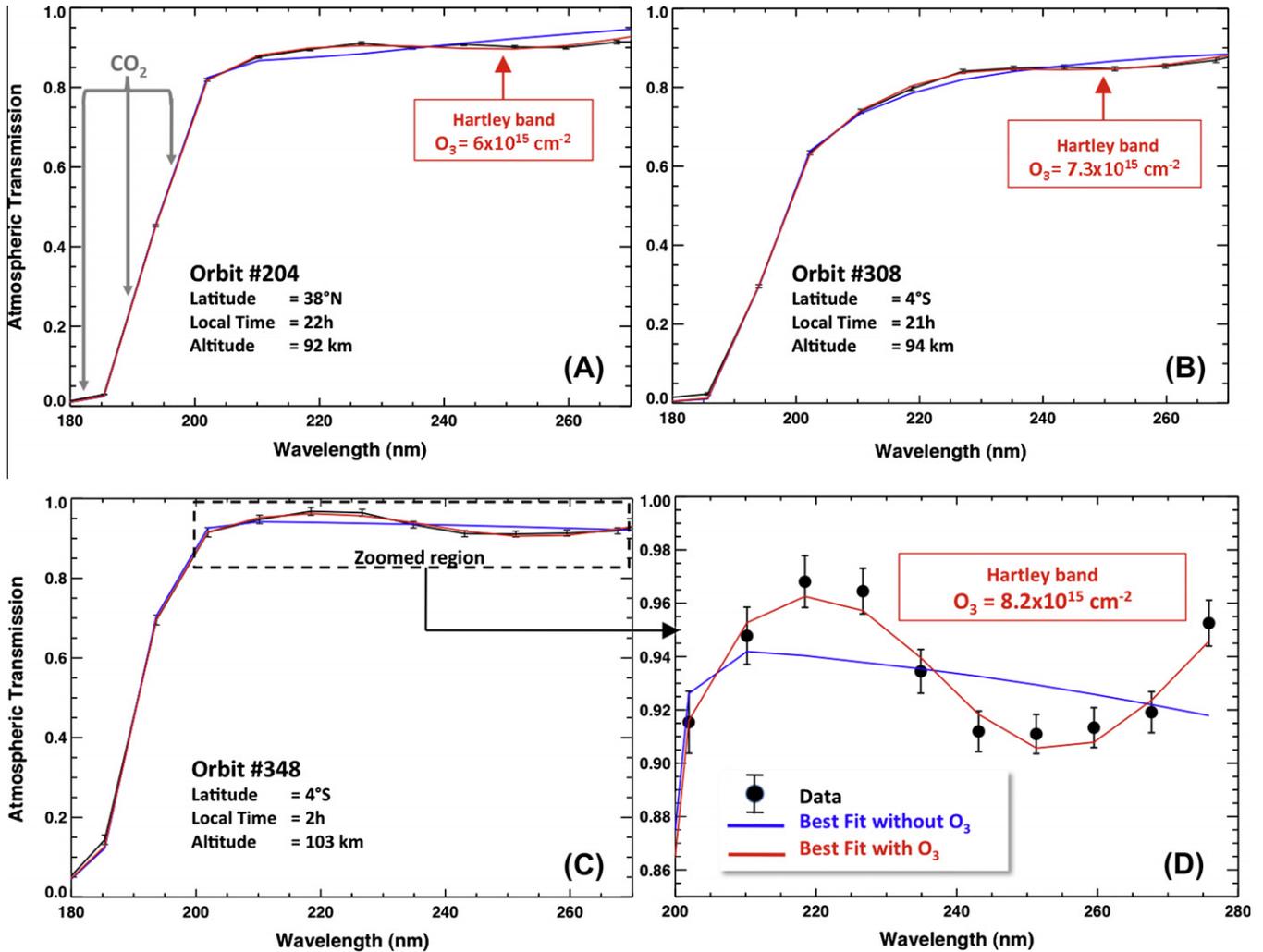


Fig. 1. From (A–C), a sample of SPICAV spectra (black dots with error bars) smoothed with a 8 nm-width running average for three different orbits at altitudes around 100 km where O_3 has been positively identified. Occultation retrieval uses a Levenberg–Marquardt algorithm to solve for gaseous and aerosols quantities simultaneously at each altitude. The $1 - \sigma$ confidence level for ozone signature is typically produced by an abundance of $5\text{--}10 \times 10^{14}$ molecules cm^{-2} . The blue curve indicates spectral inversion best fit without ozone (CO_2 and aerosols only), while the red curve shows the best fit with ozone Hartley band included. Plot (D) is a zoomed version of the 200–280 nm range of (C) to emphasize the prominent ozone signature. CO_2 absorption creates a sharp drop of transmission below 200 nm (gray arrows in A). Data inversion without ozone (blue curves) is unable to reproduce the transmission feature between 220 and 280 nm, resulting in a spectrally flat continuum across the O_3 absorption range.

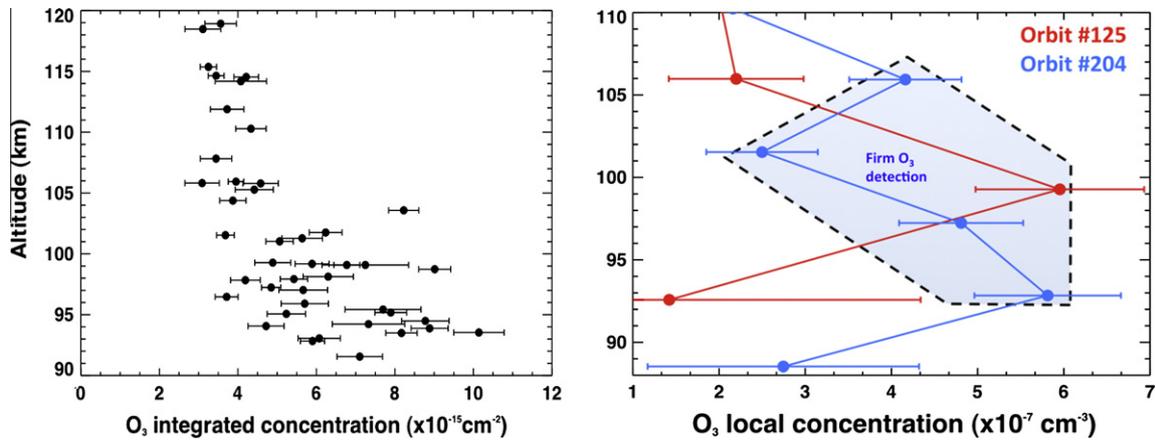


Fig. 2. (Left) A synthesis of all positive detections of ozone on Venus made by SPICAV as a function of altitude. Most detections concentrate between 90 and 105 km, being on the average at 99 km, with a few outlying points located above 110 km. The lack of ozone signature in the spectra collected above and below the detection altitude implies that the bulk of O_3 molecules lies within a layer not exceeding 5–10 km in thickness. (Right) Ozone concentration profiles for two different orbits. Profiles have been obtained after inversion of the slant ozone densities displayed in the left plot. Units are in molecules cm^{-3} . Points associated with a firm detection (confidence level $>5\sigma$) are framed by the light blue shaded area. Both profiles show that ozone peaks between 90 and 100 km, decreasing above and below, indicating a distinct layered shape.

2010). During the night, O_3 formation via the $O_2 + O$ reaction is balanced by its loss through the following main reactions:



Reaction (4), which constitutes part of the Bates–Nicolet mechanism, has been advocated to explain the OH emission feature in the near-infrared (at 1.46 and 2.81 μm) observed by VIRTIS on Venus Express (Piccioni et al., 2008; Migliorini et al., 2010; Soret et al., 2010). The OH (1–0) Meinel band emits at an average altitude of 96 km. This is consistent with our measurements which indicate a detection altitude for ozone varying between 90 and 120 km with a mean value of 99 km (Fig. 2-left). The product of concentrations of ozone with hydrogen required to match OH emission is of $4\text{--}9 \times 10^{15} \text{ cm}^{-6}$. With a hydrogen density predicted of around

10^8 cm^{-3} (Yung and DeMore, 1999), the required ozone density should be $4\text{--}9 \times 10^7 \text{ cm}^{-3}$ (note however that this crude estimation makes no case of the potential influence of quenching-led deexcitation process), lying in the same range as the concentrations reported here.

The spatial distribution of our ozone detections does not exhibit any specific pattern (Fig. 3). The OH (1–0) emission distribution reported by VIRTIS is similarly featureless, suggesting an overwhelming influence of chemistry over transport (Piccioni et al., 2008; Migliorini et al., 2010). Essentially found in the evening side of the southern hemisphere, ozone detections are scattered between the equator and $\sim 40^\circ S$. The uneven coverage of SPICAV occultation is not suited to reliably address temporal and spatial variability, yet the absence of firm O_3 detections at the anti-solar point is a puzzling feature of our dataset. The formation of ozone depends primarily on the availability of oxygen atoms and molecules and as such, may be expected to correlate with $O_2(^1\Delta)$ nightglow emission which concentrate in the anti-solar region near 96 km (Drossart et al., 2007; Piccioni et al., 2009). O_2 nightglow results from the recombination of oxygen atoms that originate from the dayside through CO_2 photolysis and that are further advected by the sub-solar-to-antisolar (SSAS) thermospheric circulation. A possible explanation for the

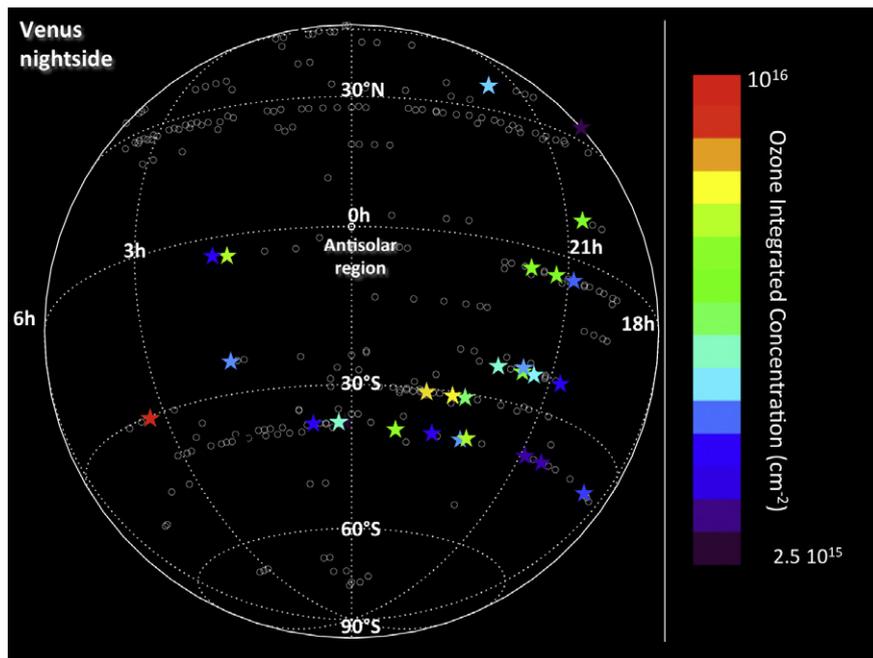


Fig. 3. Nightside view of Venus showing the ozone detections of SPICAV. Positive identifications are indicated by stars with a color code scaled to the ozone abundance integrated along the line of sight (molecules cm^{-2}). Empty circles point the location of all successful occultation performed between April 2006 and July 2010, without positive detection. As noted for the observations of the OH emission with VIRTIS (Piccioni et al., 2008; Migliorini et al., 2010; Soret et al., 2010), ozone shows no obvious maximum in column abundance in the antisolar region where the thermospheric circulation subsides and the O_2 airglow emission concentrates.

lack of O₃ detection in the antisolar region is the presence in the SSAS of large amounts of chlorine radicals produced on the dayside by the photolysis of HCl (Yung and DeMore, 1999). Reaction (6) of O₃ with chlorine is in principle the dominant loss term for ozone (Yung and DeMore, 1999; Krasnoposly, 2010). Consequently, the potentially chlorine-rich airmasses of the subsiding circulation in the antisolar region might prevent the buildup of measurable amounts of O₃. Ozone destruction might also be intensified if the adiabatically warmed environment of the descending branch of the SSAS (Bertaux et al., 2007; Bailey et al., 2008) due to the temperature dependence of reaction (6). The model of Yung and DeMore (1999) predicts that ozone vertical distribution is maximal at 96 km with a second peak near 65 km. Below 75 km however, the stellar signal is lost due to the presence of the opaque sulfuric acid aerosols. A secondary peak at 65 km, if it exists can thus not be sampled by SPICAV. The altitude of the main peak along with their estimate for concentration of $1\text{--}2 \times 10^7 \text{ cm}^{-3}$ is in line with our measurements. These values do however conflict with the nightside photochemical model of Krasnoposly (2010) which predicts 200 times more ozone and exhibits a very sharp peak. The latter appears controlled by the shapes of the corresponding predicted O and O₂ profiles (displayed in his Fig. 8), showing an abrupt decrease of O atoms below 90 km and a more gradual decrease of O₂ above that level. The ozone overestimation in Krasnoposly's model likely results from specifying a chlorine concentration weaker than Yung and DeMore (1999).

Our observations thus bring new evidence that the equilibrium of oxygen species in the upper atmosphere of Venus is dominated by the same chlorine-catalyzed destruction cycles that prevails in Earth's stratosphere. This underlines the importance of day to night circulation in the upper atmosphere and its coupling with chemistry when thermospheric air containing O, Cl and N atoms descends on the night side. Together with O₂ 1.27 μm and NO γ and δ bands (Gérard et al., 2008), our observations of ozone will constrain 3D models of this region of Venus. The direct relation between ozone and molecular oxygen makes ozone a unique proxy for estimating O₂ abundance in planetary atmospheres, which is otherwise challenging to detect directly (except for an absorption feature at 761 nm; Kaltenegger et al., 2007). In the field of exoplanets, the O₃–CO₂–O₂ triplet detection is considered to be a robust biomarker signature that can be used to distinguish between abiotic and biotic production of oxygen (Selsis et al., 2002; Segura et al., 2007). For Mars, Selsis et al. (2002) estimated that an ozone concentration greater than 20% of the Earth's value would be needed to establish the existence of biological oxidizing agents. Our observations contribute to the growing characterization of the atmospheric composition of the Solar System bodies, and show that on Venus as on Mars, the positive identification of this triplet is not associated with a biological activity on this planet. The Venusian ozone layer that is reported here appears too tenuous (>0.02 DU, value obtained after vertical integration of the local concentrations measured by SPICAV) to efficiently filter out UV radiation and protect organisms if they were to develop below. On Earth, emerging life eventually modified its environment, disrupting chemical equilibrium in a sustainable manner: oxygen photosynthesized by cyanobacteria eventually led to the formation of an optically thick and thus protective layer of ozone. Such a positive feedback has not occurred on Venus or Mars, or if it has, eventually vanished.

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