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Composition of the atmosphere of Venus below the clouds

Bruno Bézard¹ and Catherine de Bergh¹

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[1] The composition of Venus' lower atmosphere, beneath the clouds, has been investigated through both in situ measurements and remote-sensing observations. In 1978 the mass spectrometers and gas chromatographs aboard the Venera 11–12 landers and Pioneer Venus Large probe returned unique information on the abundances of carbon dioxide, nitrogen, noble gases, and other minor species. Radio occultations from the Pioneer and Magellan spacecraft provided measurements of the vertical profile of sulfuric acid vapor. In the 1980s and 1990s the discovery of near-infrared emission from the night side of Venus, through narrow spectral windows in the 0.9–2.5 micron region, opened a new opportunity of probing the lower atmosphere and surface. The abundances of water vapor, halides, carbon monoxide, sulfur dioxide, and carbonyl sulfide were determined, as well as the deuterium-to-hydrogen ratio. The vertical profile of water vapor in the 0- to 45-km-altitude range and the CO and OCS mean vertical gradients in the 30- to 40-km region have been determined from various analyses. In addition, evidence for latitudinal variations of these two species was found from Galileo and recent ground-based nightside observations. Conflicting results have been reported on the SO₂ abundance below 35 km and on the H₂O profile below 20 km. The whole set of available measurements provides important constraints on the chemistry and dynamics of Venus' lower atmosphere. However, key information is still missing, including the abundances of CO and sulfur compounds near the surface, composition maps at high latitudes, and possible small-scale and temporal variability of trace compounds.

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1. Introduction

[2] The lower atmosphere of Venus, beneath the sulfuric acid cloud decks, can be investigated by only a limited number of means. First of all, atmospheric sensors aboard entry probes in the 1970s and 1980s provided unique information on the temperature and composition. The Venera 11–12 and Pioneer Venus Large Probe carried mass spectrometers and gas chromatographs which directly sampled the abundances of various gases at different altitudes (see review by *Von Zahn et al.* [1983]). Spectro-photometers aboard the Venera 11, 13, and 14 probes scanned the range 0.4–1 μm throughout the descent, allowing for determination of the water vapor abundance profile [*Moroz*, 1983; *Ignatiev et al.*, 1997]. The Vega 1 and 2 entry probes in 1985 recorded absorption spectra of the atmosphere in the range from 220 to 400 nm using a ultraviolet spectrometer with a light source (ISAV). Vertical profiles of sulfur dioxide (SO₂) were derived along with information on the aerosol and cloud structure [*Bertaux et al.*, 1996].

[3] Remote sensing of the deep atmosphere is possible at centimeter wavelengths either from ground-based radio telescopes or from radio occultation experiments aboard

spacecraft. Multifrequency measurements with the Very Large Array (VLA) have provided constraints on sulfuric acid vapor (H₂SO₄), the dominant microwave absorber, between approximately 35 and 55 km [*Jenkins et al.*, 2002]. The Mariner 10 and Magellan radio occultation experiments yielded vertical profiles of H₂SO₄ in about the same altitude range but with a much better vertical resolution [*Jenkins et al.*, 1994; *Kolodner and Steffes*, 1998]. Sulfur dioxide also absorbs at centimeter wavelengths, more at X-band than at S-band, so that some constraints on its abundance can be placed from the above measurements.

[4] Finally, as detailed in section 2, thermal emission from the sub-cloud atmosphere can be detected on the night side in narrow infrared windows. Spectral analysis of this emission, originally detected by *Allen and Crawford* [1984], offers a unique opportunity to investigate remotely the composition of the deep atmosphere. A first review of the results obtained from various studies up to the mid-1990s has been presented by *Taylor et al.* [1997].

[5] Carbon dioxide (96.5%) and nitrogen (3.5%) are by far the most abundant gases in the lower atmosphere of Venus. Noble gases and a series of chemically active species have also been detected, including water vapor, sulfur-bearing gases and halides. We review here our knowledge on these active compounds related to the complex sulfur cycle at work on Venus, the formation of the sulfuric acid clouds and the surface-atmosphere interactions. The Venus

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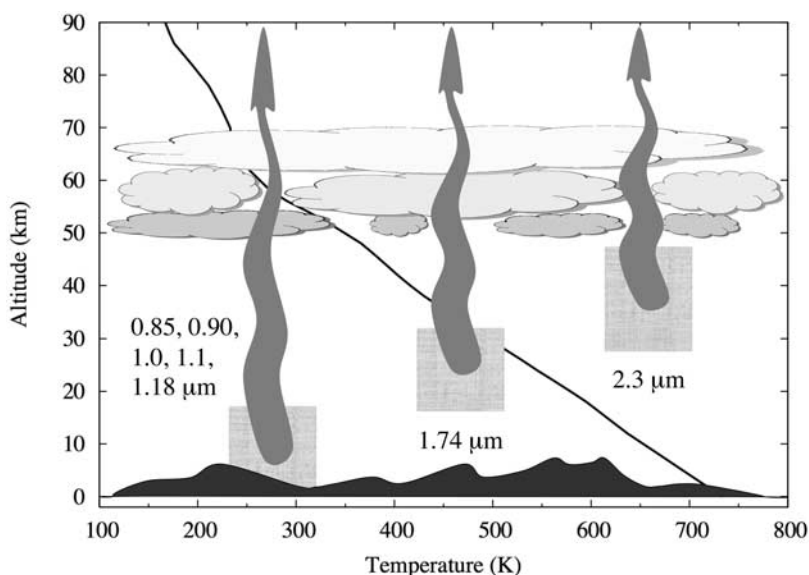


Figure 1. A schematic of Venus' atmosphere showing the temperature profile, location of the cloud layers, and nightside thermal emission in the near-infrared windows.

International Reference Atmosphere (VIRA) was published in 1985, after the extensive exploration of Venus by the Venera and Pioneer Venus spacecrafts [Von Zahn and Moroz, 1985]. We present updates to this model, based on the information gathered from the re-analysis of in situ probe data, microwave measurements and nightside investigations. The successful orbit insertion of the Venus Express spacecraft, more than a decade after the Magellan mission (1990–1994) and two decades after the Vega 1 and 2 missions in 1985, makes this review particularly timely. A more general review of the composition of Venus below 100 km has also been recently published by *de Bergh et al.* [2006].

2. Near-Infrared Nightside Windows

[6] A series of narrow atmospheric windows, located between the strong bands of CO_2 and H_2O , take place in the near-infrared region and can be detected on the night side. They are centered at 2.3, 1.74, 1.31, 1.27, 1.18, 1.1, 1.0, 0.90 and 0.85 μm . Shortward of 2.5 μm , sulfuric acid, the main constituent of the cloud particles, is almost non-absorbing and a fraction of the thermal emission from the hot deep atmosphere can then escape the atmosphere in these windows, leaking through the clouds (Figure 1). In the core of the windows, the major source of gaseous opacity is pressure-induced CO_2 bands and the far wings of allowed nearby CO_2 bands (see *Tonkov et al.* [1996] for the 2.3- μm region). Gas opacity generally decreases with decreasing wavelength and the transparency of the windows accordingly increases, allowing emission from the surface to escape below 1.2 μm , as attested by observations and radiative transfer modeling [Taylor et al., 1997].

[7] The broadest and most complex window extends from 2.20 to 2.50 μm and probes the altitude range 26–45 km [Pollack et al., 1993]. It shows signatures from CO , H_2O and HDO , CO , OCS , SO_2 and HF (Figure 2). The 1.74- μm window probes deeper, approximately 15–30 km, and exhibits absorption features from CO_2 , H_2O and the two main isotopes of HCl (H^{35}Cl and H^{37}Cl) [Bézar et al.,

1990; Pollack et al., 1993]. A narrow window takes place at 1.31 μm ; limited on both sides by strong CO_2 bands, it does not show signatures from other compounds and is more opaque than the other windows. At 1.27 μm , thermal emission from the 15- to 30-km range is detected, forming a continuum over which strong airglow emission from O_2 at high altitudes is seen [e.g., Crisp et al., 1996]. This airglow was originally detected by Connes et al. [1979] on both the day and night sides of the planet. At high spectral resolution, a HF line can be detected in this window. The 1.18- and 1.10- μm windows are bounded on one side by CO_2 bands and on the other side by the wings of the 1.13- μm water vapor band. A large fraction of the emission (40 and 60%, respectively) originates from the surface [Meadows and Crisp, 1996]. These two windows can be used to determine the water abundance in the lowest scale height of the atmosphere. The 1.0- μm window, with essentially all the emission coming from the surface and practically no gas absorption, is the most suitable for surface studies. Finally, two weak windows occur at 0.85 and 0.90 μm , interlaced with the H_2O bands at 0.95 and 0.82 μm and the CO_2 band around 0.87 μm [Baines et al., 2000]. Spectral observations of these nightside windows have greatly improved our knowledge of Venus' composition below the clouds, as illustrated below.

3. Carbon Monoxide

[8] In situ measurements by gas chromatographs aboard the Pioneer Venus and Venera 12 spacecraft have sampled the CO abundance below the clouds of Venus. The former yielded 20 ± 3 ppm at 22 km and 30 ± 18 ppm at 42 km [Oyama et al., 1980] and the latter 28 ± 7 ppm at 36–42 km and 17 ± 1 ppm at 12 km [Gel'man et al., 1979]. Despite the large error bars above 36 km, these measurements indicate an increase of the CO mixing ratio with altitude (Figure 3). This trend is continuing at higher altitudes with a mixing ratio of about 50 ppm inferred from ground-based measurements at the cloud tops [Connes et al., 1968; Young, 1972].

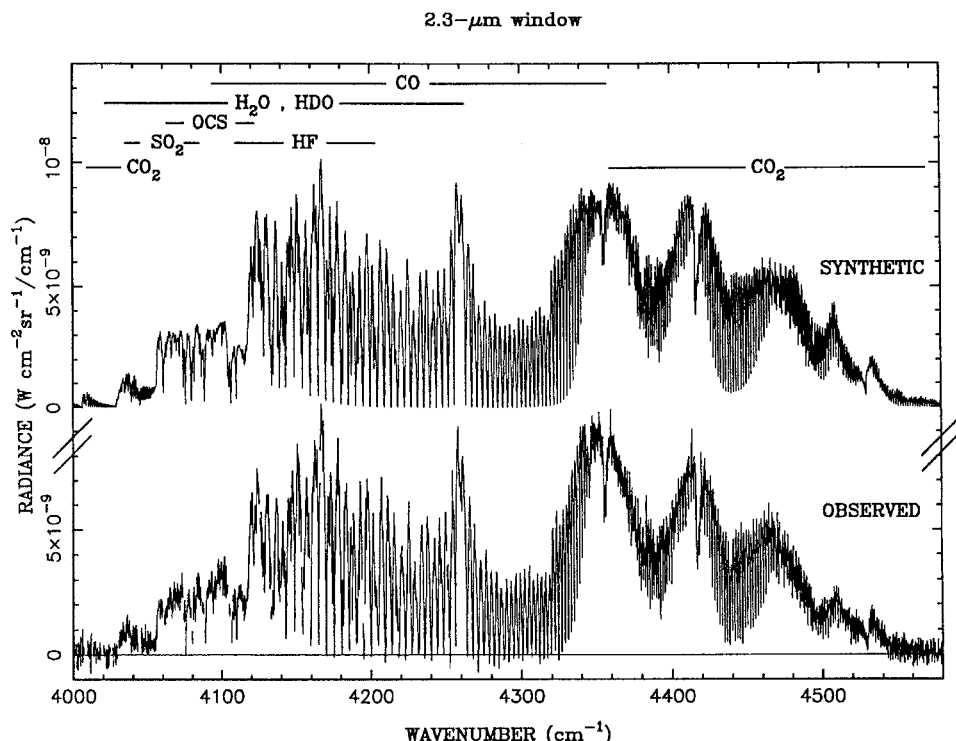


Figure 2. High-resolution (0.15 cm^{-1}) spectrum of the $2.3\text{-}\mu\text{m}$ nightside window recorded at the Canada-France-Hawaii Telescope. Absorption features from CO_2 , H_2O , HDO , CO , HF , OCS , and SO_2 are detected. From *Taylor et al.* [1997]; reprinted by permission of the University of Arizona Press.

More recently, nightside investigations confirmed the CO gradient in the lower atmosphere. As first demonstrated by *Pollack et al.* [1993], the (2-0) CO band in the $2.30\text{--}2.42 \text{ }\mu\text{m}$ region provides vertically resolved information over approximately the interval $28\text{--}42 \text{ km}$. Compiling various studies,

the CO mixing ratio at 36 km can be estimated as $26 \pm 5 \text{ ppm}$ [*Pollack et al.*, 1993; *Bézard*, 1994; *Marcq et al.*, 2006] and the concentration gradient in the $28\text{--}42 \text{ km}$ interval as $0.6 \pm 0.4 \text{ ppm km}^{-1}$ [*Taylor et al.*, 1997; *Marcq et al.*, 2006]. The observed gradient implies a source above the clouds, very

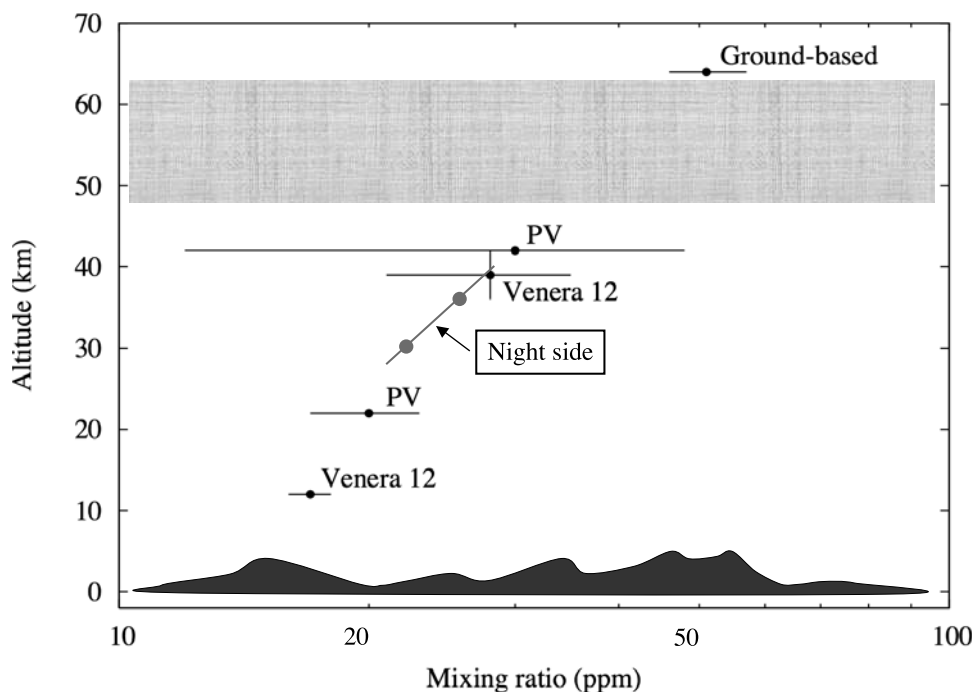


Figure 3. Measurements of the CO mixing ratio from Pioneer Venus (PV), Venera 12, and ground-based nightside and dayside observations.

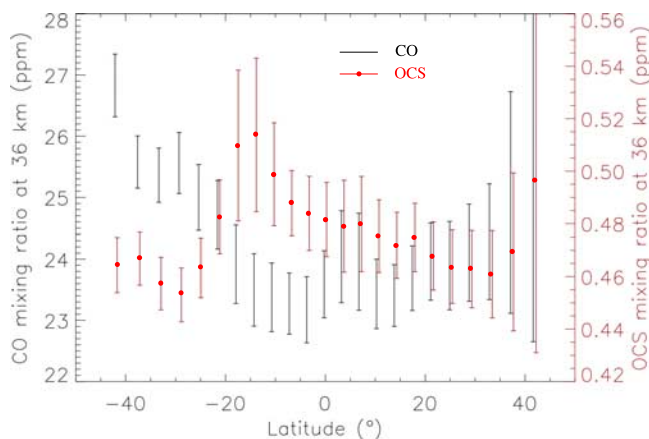


Figure 4. Latitudinal variations of CO and OCS at 36 km in the range 40°S–40°N as inferred from ground-based spectro-imaging data in the 2.3- μ m nightside window [Marcq *et al.*, 2006].

likely CO₂ photodissociation, and a sink near the surface. This sink is thought to be the formation of OCS, through reaction of CO either with SO₂ [Pollack *et al.*, 1993] or more likely with S₂, as advocated by Hong and Fegley [1997].

[9] 2.3- μ m nightside observations also give evidence for horizontal variations in the CO abundance below the clouds. NIMS spectra recorded during the Galileo flyby of Venus in February 1990 indicate an increase of about 35% north of 47°N compared to the 55°S–30°N region [Collard *et al.*, 1993]. Due to the geometry of the observations, the NIMS data do not allow us to know if a similar enhancement exists in the southern polar region. More recently, Marcq *et al.* [2005a, 2006] observed Venus' night side in the same window using the SpeX spectro-imager at the NASA Infrared Telescope Facility (IRTF). Mapping the 40°S to 40°N region, they derived an increase by $12 \pm 4\%$ of the CO mixing ratio around 36 km between the equator and 40°S (Figure 4) and a concomitant increase of the vertical gradient by a factor of ~ 2 (albeit with large error bars). The increase of CO north and south of the equatorial region can be interpreted in the framework of general circulation models with Hadley cells rising at the equator and descending at high latitudes. Downwelling brings air enriched in gases formed at high altitudes, such as CO, to lower atmospheric levels, therefore increasing their mixing ratios at these levels. An opposite behavior is expected for gases showing a decreasing-with-height mixing ratio, as illustrated below.

4. Carbonyl Sulfide

[10] Carbonyl sulfide (OCS) was first unambiguously detected from high-resolution nightside observations in the 2.3- μ m window [Bézard *et al.*, 1990]. As shown by Pollack *et al.* [1993], the spectral data allow the retrieval of mixing ratios around 38 km from the core of the absorption feature at 2.43 μ m, and around 30 km from the low-wavelength wing of the band near 2.42 μ m (see, e.g., Figure 5). The best fit abundances derived from various investigations are 0.35 ± 0.1 ppm at 38 km and a range of 10–20 ppm at 30 km [Taylor *et al.*, 1997]. The OCS vertical profile thus exhibits a strong negative gradient in the altitude range 30–40 km with a

mixing ratio scale height equal to 0.2 ± 0.05 times the pressure scale height [Marcq *et al.*, 2006]. The implied sink of OCS in this region is thought to be reaction with SO₃, produced by thermal decomposition of H₂SO₄, to form CO, S₂ and SO₂ [Krasnopolsky and Pollack, 1994]. Thermochemical models thus support the idea that the coupled decrease in OCS and increase of CO observed from 30 to 40 km results from CO formation at the expense of OCS.

[11] Horizontal variations of OCS have recently been inferred from SpeX/IRTF spectro-imaging observations. Assuming no change in the vertical gradient of OCS, Marcq *et al.* [2005a] concluded to a $\sim 10\%$ decrease of the OCS abundance from the equator to 40°S. Solving for both the 36-km mole fraction and the 30- to 37-km gradient, Marcq *et al.* [2006] concluded that, southward of 20°S, OCS is depleted above 35 km but enriched at 30–33 km. Therefore the OCS variation in latitude is anti-correlated with that of CO around 36 km, with both molecules exhibiting more shallow gradients near the equator. Because the two

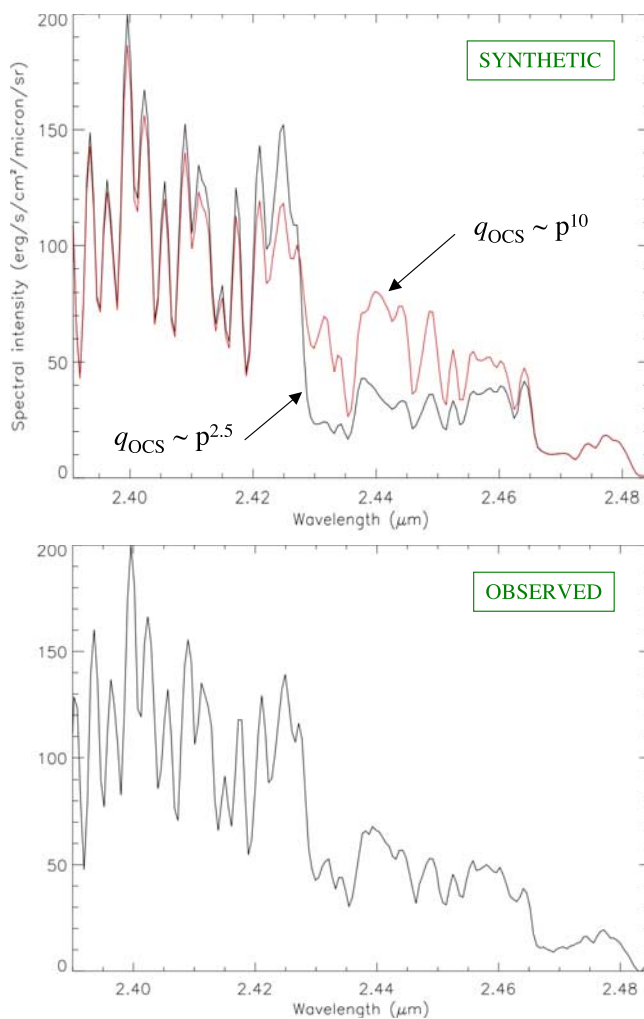


Figure 5. (bottom) Ground-based observations of the OCS band in the 2.3- μ m nightside window at a resolving power of 2000. (top) Synthetic spectra with two different profiles of OCS having a mixing ratio (q_{OCS}) scale height of 0.4 and 0.1 times the pressure (p) scale height (adapted from Marcq *et al.* [2006]).

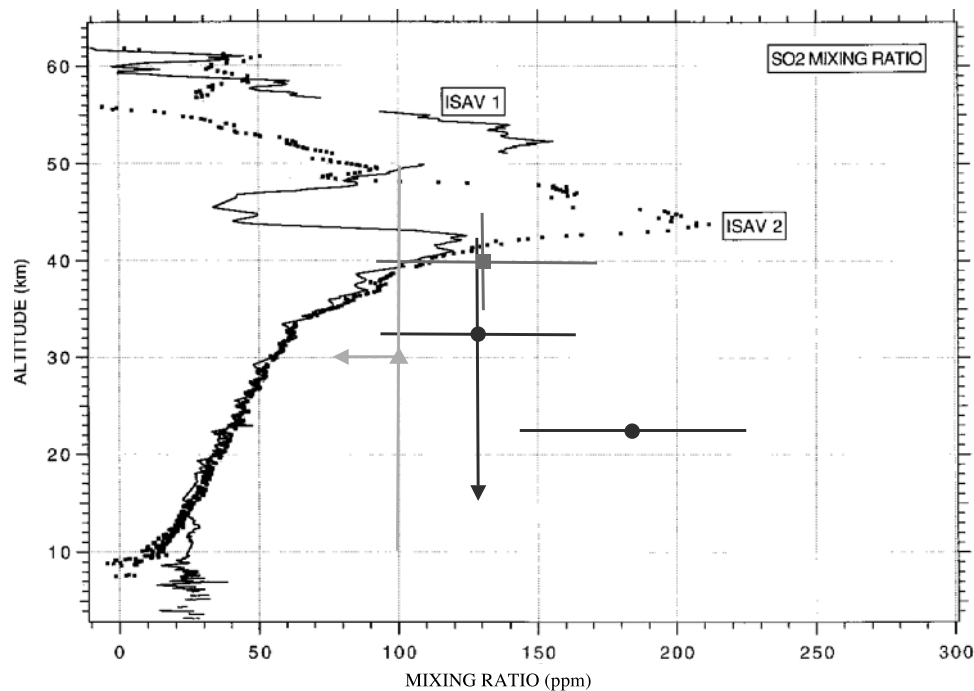


Figure 6. Vertical profiles of SO_2 determined by the ISAV experiment aboard Vega 1 and 2 [Bertaux *et al.*, 1996]. The circles indicate the Pioneer Venus and Venera 12 GC measurements, the square indicates the $2.3\text{-}\mu\text{m}$ nightside observations [Bézard *et al.*, 1993], and the triangle indicates the upper limit from microwave flux measurements [Jenkins *et al.*, 2002].

compounds have opposite vertical gradients, this behavior is likely the signature of the general circulation, with rising motion at equatorial latitudes (and descending air at high latitudes). The larger abundance of OCS below ~ 33 km south of 20°S may result from the larger abundance of CO leading to enhanced production of OCS in the lower atmosphere.

5. Halides

[12] Nightside observations have provided the first measurements of two halides (HF and HCl) below the clouds [Bézard *et al.*, 1990]. Several HF lines can be detected in high-resolution spectra of the $2.3\text{-}\mu\text{m}$ window probing the 30–40 km range, while strong HCl lines are prominent in the $1.74\text{-}\mu\text{m}$ window originating from the 15–30 km region. The derived mixing ratios are 5 ± 2 ppb and 0.5 ± 0.15 ppm, respectively [Taylor *et al.*, 1997]. These values are similar to those measured at the cloud tops 20 years before by Connes *et al.* [1967]. This constancy with altitude and over time suggests that these two corrosive gases are in chemical equilibrium rather than the result of time-variable phenomena such as volcanism. Fegley and Treiman [1992] investigated several potential minerals that can buffer their atmospheric abundances and proposed various assemblages common in terrestrial alkaline rocks that lead to the observed abundances at the temperature of Venus' surface.

6. Sulfur Dioxide

[13] Sulfur dioxide, a key actor in the sulfur cycle, has been measured in situ by various entry probes. The Pioneer Venus gas chromatograph derived a mixing ratio of $185 \pm$

43 ppm at 22 km [Oyama *et al.*, 1980] and the Venera 12 gas chromatograph determined a mean value of 130 ± 35 ppm below 42 km [Gel'man *et al.*, 1979]. Bertaux *et al.* [1996] published a detailed analysis of the data collected by the ISAV ultraviolet spectrometer aboard the Vega 1 and 2 probes. The two probes descended into Venus' atmosphere on 11 and 15 June 1985 at two different locations (7.5°N – 177.7°E and 8.5°S – 164.5°E , respectively). SO_2 profiles, obtained from the cloud tops down to the surface, show a double peak at 51.5 and 42.5 km (150 and 125 ppm, respectively) for ISAV1, and a single peak at 43 km (210 ppm) for ISAV2. Below, the two profiles exhibit the same pronounced decrease: 56 ppm at 32 km, 38 ppm at 22 km and 20–25 ppm at 12 km (Figure 6).

[14] The SO_2 band present in the $2.3\text{-}\mu\text{m}$ window has been used to determine the abundance of this gas in the 35–45 km region using nightside spectroscopy [Bézard *et al.*, 1993]. The derived abundance (130 ± 40 ppm) agrees with the Pioneer Venus and Venera 12 gas chromatograph (GC) measurements in 1978. This stability over time contrasts with the apparent decline observed at the cloud tops since these missions [Esposito *et al.*, 1997]. While the ISAV profiles are in good agreement with the nightside results relating to 35–45 km, they conflict with the GC determinations at lower altitudes.

[15] Microwave wavelengths are somewhat sensitive to SO_2 opacity, and 1.3- and 2-cm maps obtained with the Very Large Array (VLA) seem to suggest low SO_2 mixing ratios below the clouds: less than 100 ppm at low latitudes and less than 50 ppm in polar regions [Jenkins *et al.*, 2002]. However, the sensitivity of the microwave flux to SO_2 is limited and the derived constraints strongly depend on the

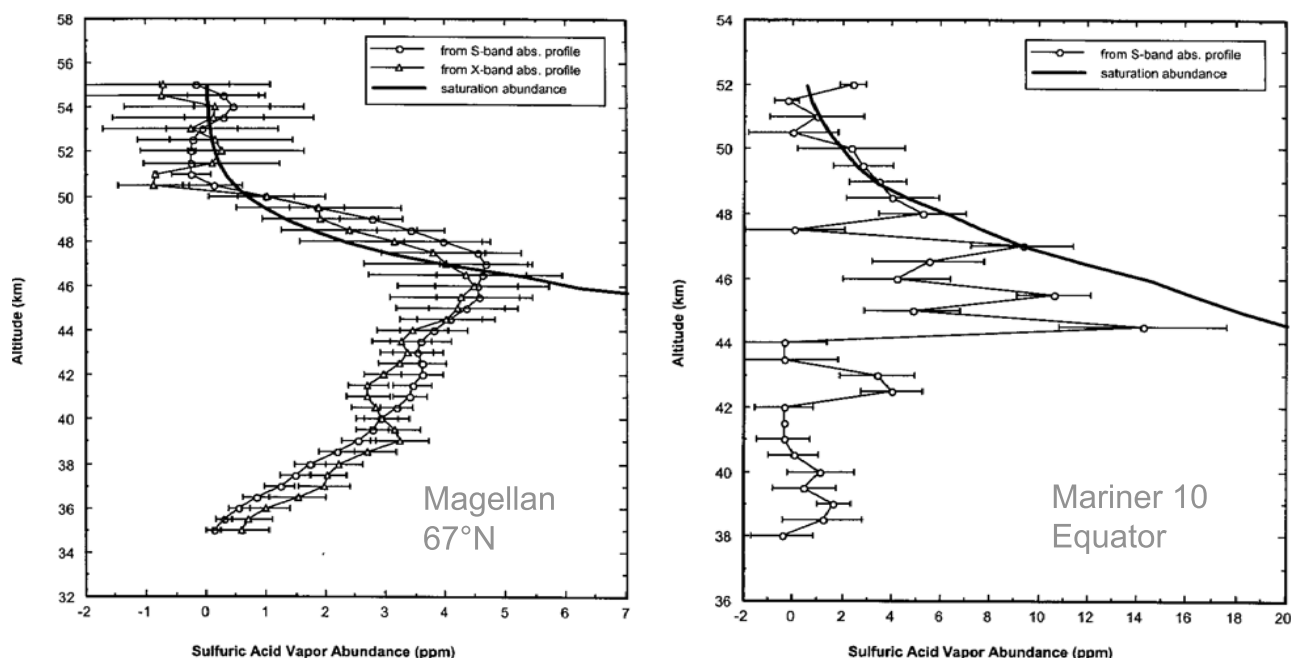


Figure 7. Vertical profiles of H_2SO_4 vapor obtained with the Magellan and Mariner 10 radio occultation experiments at 67°N latitude and the equator, respectively. The solid line represents the saturation profile [Kolodner and Steffes, 1998].

assumed temperature profile. They also might be affected by uncertainties in the measurement calibration and in the SO_2 absorptivity at the relevant temperatures and CO_2 pressures.

[16] Fegley and Treiman [1992] have shown that chemical reactions with surface minerals cannot buffer the SO_2 abundance in the lower atmosphere because of their extremely low kinetics. The gradient in the ISAV profiles below 40 km would thus require the transformation of SO_2 into another sulfur-bearing gas in the lower atmosphere. The fact that this putative abundant gas is still undetected and that existing thermochemical models do not reproduce such a SO_2 depletion casts doubt on the ISAV profiles, which in addition rely on a number of assumptions made in this complex data analysis. The ISAV results clearly need to be confirmed by future in situ experiments, given the strong implications they would have on Venus' sulfur chemistry.

7. Sulfuric Acid Vapor

[17] Gaseous H_2SO_4 was detected from data recorded with the Pioneer Venus radio occultation experiment at a wavelength of 13 cm [Jenkins and Steffes, 1991]. Despite quite large error bars, the abundance profiles derived from the absorptivity profiles suggest significant latitudinal variations in the abundance of H_2SO_4 between the equatorial region and latitudes above 35°N , with generally lower values at high latitudes. The Magellan radio occultation measurements in 1991–1992 provided a set of H_2SO_4 profiles at high northern and southern latitudes with a much better accuracy [Jenkins *et al.*, 1994; Kolodner and Steffes, 1998]. Data at 67°N indicate mixing ratios of 3–7 ppm below the cloud base at 47 km, with a sharp drop off below 39 km (Figure 7). At 88°S , a 6–10 ppm abundance is derived below the cloud base at 44 km and no information is available below 41 km. A

reanalysis of the Mariner 10 radio occultation results by Kolodner and Steffes [1998] yields a sub-cloud abundance of 10–14 ppm below 48 km at the equator and a sudden drop off below 45 km (Figure 7). The differences between the derived profiles indicate variations in gaseous H_2SO_4 with latitude, longitude and possibly time. At some specific locations, the differences in the H_2SO_4 abundances retrieved from S- and X-band data suggest an elevated amount of another constituent, most likely SO_2 .

[18] Jenkins *et al.* [2002] conducted radio observations with the VLA at 1.3 and 2 cm to investigate horizontal and vertical variations of temperature and H_2SO_4 abundance. At high latitudes (beyond 45°), the H_2SO_4 profile peaks around 46 km with a mixing ratio of about 8 ppm, and decays rapidly away from this altitude. The results are generally consistent with the Magellan profiles. At low latitudes, no significant H_2SO_4 is observed with an upper limit of 2.5 ppm, well below that derived from Mariner 10 radio occultation data (Figure 7).

[19] The sharp drop off in the H_2SO_4 mixing ratio observed a few kilometers below the cloud base is consistent with the expected thermal decomposition of this gas into SO_3 and H_2O [Prinn, 1978]. The whole set of available measurements indicates large spatial and temporal variations that likely result from dynamical processes.

8. Other Sulfur Compounds

[20] Strong absorptions in the 450–600 nm range observed in situ by the Venera 11 and 12 probes between 10 and 30 km have been interpreted as due to trace amounts of gaseous elemental sulfur [Moroz *et al.*, 1979]. Among all the sulfur allotropes that could exist in the lower atmosphere (S_n , for $n = 1$ to 8), only S_3 absorbs significantly near 450 nm. Moroz *et al.* [1979] used these wavelengths to derive a

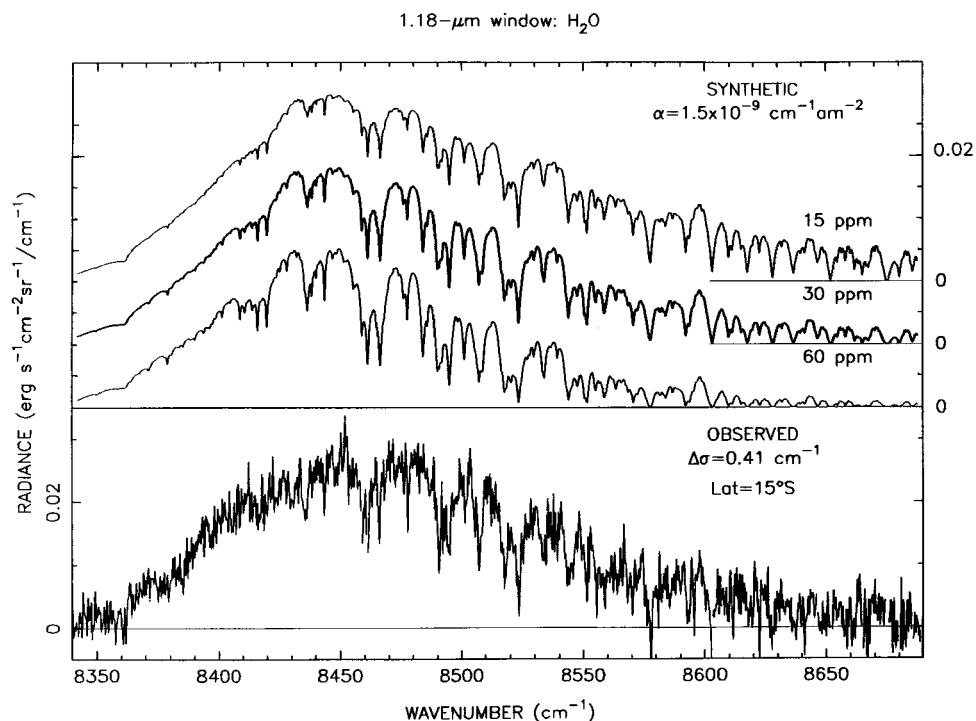


Figure 8. High-resolution (0.4 cm^{-1}) spectrum of the $1.18\text{-}\mu\text{m}$ nightside window recorded at the Canada-France-Hawaii Telescope. Absorption features from H_2O are visible beyond 8400 cm^{-1} , in the wing of the $1.14\text{-}\mu\text{m}$ H_2O band. The low-frequency wing of the window, below 8450 cm^{-1} , is shaped by CO_2 continuous absorption. Reprinted from *de Bergh et al.* [1995] with permission from Elsevier.

mixing ratio profile of S_3 that peaks at 4×10^{-11} around 23 km altitude. Using *San'ko's* [1980] calculations of the relative abundances and vertical profiles of the various sulfur allotropes, a global mixing ratio of gaseous sulfur can be derived. A value of 2×10^{-8} for sulfur allotropes taken all together is found, with S_2 being the dominant species below 30 km altitude. Further analyses of the same data set showed that the single scattering albedo at 490 nm peaked about one scale height lower than the S_3 and S_4 profiles calculated by *San'ko* [1980]. *Von Zahn et al.* [1983] suggested that this may result from photochemistry of the sulfur allotropes not considered by *San'ko* [1980]. Some of these species could be responsible for dark markings in the clouds [see, e.g., *Esposito et al.*, 1997]. It should be further noted that *Pollack et al.* [1980] have suggested that gaseous SO_2 could be partly or entirely responsible for the “unexplained” absorption in the Venera 11 and 12 data but did not publish detailed results of their computations.

[21] In any case, thermochemical equilibrium modeling does reproduce the Venera absorption profile below 12–14 km, suggesting that, in this region, the sulfur allotropes are in equilibrium with one another and not too affected by photochemistry [Fegley, 1997]. The so-derived S_2 abundance (0.02 ppm) is actually lower than the equilibrium abundance in the near-surface atmosphere of 0.2 ppm [Fegley et al., 1997], indicating that the kinetics for the exchange of elemental sulfur with other S-bearing gases is relatively slow. The measured abundance is also smaller than that of S_2 gas in equilibrium with pyrite and pyrrhotite (0.7 ppm at 733 K and 95 bar), indicating that pyrite is not stable on Venus [Fegley, 1997].

[22] Data from the Pioneer Venus mass spectrometer [Hoffman et al., 1980; Donahue and Hodges, 1993] suggest detection of H_2S with a mixing ratio of 3 ± 2 ppm below 20 km whereas the gas chromatograph provided an upper limit of 2 ppm [Oyama et al., 1980]. This value is at least an order of magnitude larger than predicted by thermochemical equilibrium at the surface (0.1 ppm) [Fegley et al., 1997]. If H_2S is actually present in Venus' lower atmosphere at the ppm level, it would probably require a surface source, such as reaction of H_2O with pyrrhotite or volcanic outgassing, and slow gas-phase kinetics.

9. Water Vapor and D/H Ratio

[23] Water vapor measurements by entry probes below the clouds have provided conflicting results, differing by more than two orders of magnitude [Von Zahn et al., 1983; Taylor et al., 1997]. The situation cleared up with spectroscopic investigations of the nightside emission published in the 1990s [Bézard et al., 1990; Crisp et al., 1991; Pollack et al., 1993; de Bergh et al., 1995]. Water vapor absorbs in the 2.3-, 1.74-, and $1.18\text{-}\mu\text{m}$ windows (Figures 1 and 8), allowing the retrieval of a vertical profile from about 45 km down to the surface. As reviewed by Taylor et al. [1997], a consensus has emerged toward a mixing ratio of 30 ± 10 ppm approximately constant in the whole 0–45 km range. Venus' lower atmosphere thus appears globally extremely dry, much drier than indicated by the GCMS in situ measurements.

[24] The range of abundances derived still leaves room for possible vertical variations. From spectro-imaging data recorded at the Anglo-Australian Telescope (AAT) in the

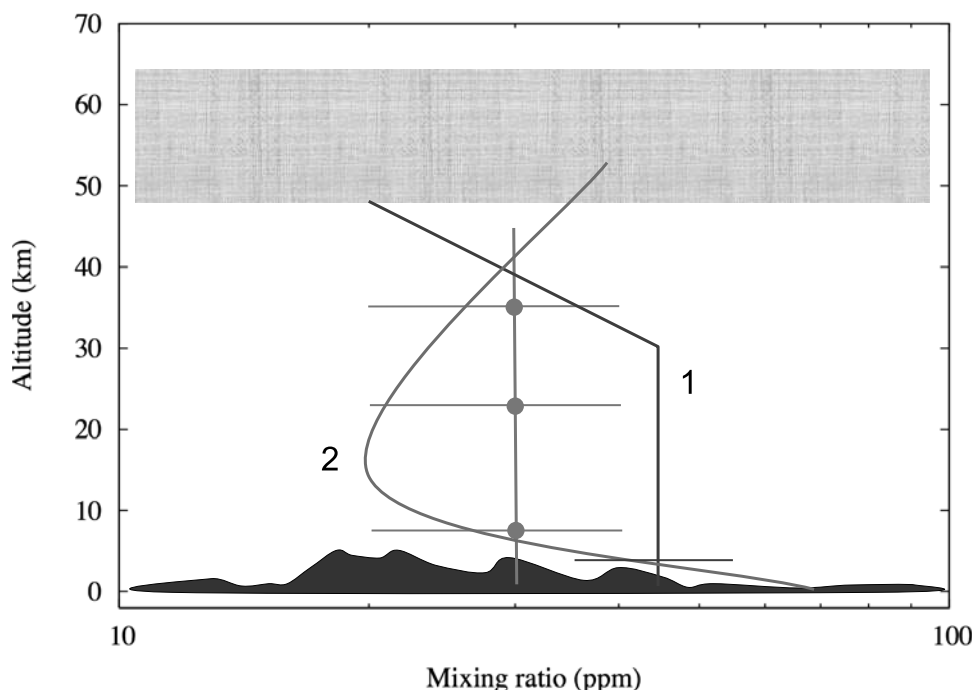


Figure 9. Determination of the H_2O mixing ratio profile from various investigations. Dots with error bars: nightside observations as compiled by Taylor *et al.* [1997]. 1, Meadows and Crisp's [1996] AAT nightside observations; 2, Ignatiev *et al.*'s [1997] reanalysis of the Venera optical spectra.

1.0, 1.1 and $1.18\text{-}\mu\text{m}$ windows, Meadows and Crisp [1996] proposed a profile that increases from 20 ppm at the cloud base to 45 ± 10 ppm from 30 km to the surface (Figure 9). Reanalyzing the Venera 11, 13 and 14 optical spectra recorded during the descents, Ignatiev *et al.* [1997] suggested a decrease of the H_2O mixing ratio from 40 ppm in the clouds down to 20 ppm at 10–20 km, although a constant value of 30 ± 10 ppm from 5 to 60 km could not be excluded. They also concluded that the mixing ratio probably increases up to 50–70 ppm below 5 km (Figure 9). This gradient is at odds with the constancy (within $\pm 10\%$) of the H_2O mixing ratio derived by Meadows and Crisp [1996] in the lowest 6 km using the local topography as an altitude discriminator. The non-constancy of the H_2O profile below the cloud base would imply an atmospheric source or sink for this compound that remains to be identified. It appears thus very desirable to reach a better precision on the H_2O profile in order to settle the issue.

[25] Various observers searched for horizontal variations in the H_2O abundance using spatially resolved nightside spectra. Drossart *et al.* [1993] analyzed a sequence of Galileo/NIMS data covering overall a small area but a wide latitude range (40°S , 50°N). The $1.18\text{-}\mu\text{m}$ window was used to map the water abundance below 15 km and no variations exceeding 20% were detected. From their IRTF spectro-imaging data at $2.3\text{ }\mu\text{m}$, Marcq *et al.* [2006] did not see either any H_2O variations at 28–42 km in the range 40°S – 40°N (with an upper limit of 20%). In contrast, Bell *et al.* [1991] presented $2.3\text{-}\mu\text{m}$ spectra of Venus' night side recorded with the CGS instrument at the IRTF which indicated an enhancement by a factor of 5 in the H_2O abundance over a low cloud opacity spot. This localized observation was interpreted as a strong downdraft associated

with evaporation of H_2SO_4 droplets. Such a feature was never seen in subsequent measurements. Although this unique measurement still remains to be confirmed, it suggests the possibility that the $2.3\text{-}\mu\text{m}$ window can be used to investigate the meteorology of Venus' clouds, not only through maps of the lower cloud opacity, but also from measurements of the water vapor abundance just below the cloud base.

[26] The $2.3\text{-}\mu\text{m}$ window offers the opportunity of observing lines from both H_2O and the deuterated isotope HDO. This can be used to measure the D/H ratio below the clouds: de Bergh *et al.* [1991] derived a value of 120 ± 40 times the terrestrial SMOW value from high-resolution CFHT spectra and, more recently, Marcq *et al.* [2005b] derived a similar Earth-to-Venus ratio (130 ± 20) from SpeX/IRTF data. The first determinations of the D/H ratio date back to the in situ measurements by the neutral mass spectrometer of Pioneer Venus, the analysis of which yields $\text{D}/\text{H} = 157 \pm 30$ times the ratio in Earth's oceans [Donahue *et al.*, 1997]. Both in situ and remote-sensing determinations thus agree and point to a strong deuterium enrichment in Venus' atmosphere.

[27] This high D/H ratio is due to the removal of water vapor through photodissociation and hydrogen escape but its interpretation depends on the lifetime of water in the atmosphere. It has first been interpreted as the signature of a lost primordial ocean [McElroy *et al.*, 1982; Donahue *et al.*, 1982], which is reasonable if the lifetime of H_2O is longer than the age of the planet. However, Grinspoon and Lewis [1988] have argued that, given the small present-day amount of water in the atmosphere and the estimated hydrogen escape flux, the residence time of water is probably shorter than the age of Venus. Consequently, the water abundance could essentially reflect a balance between

Table 1. Composition of Venus' Atmosphere Below the Cloud Decks

Gas	Altitude Range	Mixing Ratio, ppm	Comments
CO	36 km below	26 ± 5 $12 + 0.38 \times z$ (km)	latitudinal variations
OCS	38 km 30 km	0.35 ± 0.1 10–20	latitudinal variations
SO ₂	35–45 km below	130 ± 40 Conflicting results (from 38 to 185 ppm at 22 km)	
S ₂	below 12 km	~ 0.02	derived from S ₃ measurements
H ₂ S	below 20 km	1–2?	
HCl	15–30 km	0.5 ± 0.15	
HF	30–40 km	0.005 ± 0.002	
H ₂ SO ₄	46 km below 39 km	4–10 ~ 0	horizontal variations
H ₂ O	0–45 km	30 ± 10	possibly varies with altitude
D/H	30–40 km	$120 \pm 40 \oplus$	

loss by escape and supply by a source. *Grinspoon and Lewis* [1988] proposed an external source from cometary infall, while *Grinspoon* [1993] proposed an internal source from volcanic outgassing, either continuous or episodic such as the catastrophic resurfacing that occurred in the past 1 Gyr. *Gurwell* [1995] proposed an alternative solution, incorporating the primordial ocean and a steady source, which succeeds in reproducing the present D/H ratio while assuming Earth-like values for the primordial ocean and the continuous source. A better assessment of the various scenarios will require an improved understanding of the past and present escape mechanisms.

10. Conclusions

[28] Table 1 summarizes our knowledge of the composition of the lower atmosphere as discussed above. In addition to the horizontal variations observed for some compounds, temporal variations are also possible. The Venus Express spacecraft, orbiting the planet since 11 April 2006, will conduct scientific observations for over two full Venusian days (486 Earth days). Instruments aboard the spacecraft will allow us to map and monitor the compounds in Table 1, except HF, H₂S and S₂. The radio science experiment VeRA will provide the H₂SO₄ vapor profile within and below the clouds at specific locations through occultation measurements. The other gases will be mapped below the clouds with the ultraviolet/visible/near-infrared mapping spectrometer (VIRTIS) using the nightside windows. In addition, the infrared channel of SPICAV (Spectroscopy for Investigation of Characteristics of the Atmosphere of Venus) will record spectra of the short-wavelength ($<1.7 \mu\text{m}$) nightside windows in its nadir observing mode. The Venus monitoring camera (VMC) may also provide some constraints on the water vapor near the surface by imaging the night side through its filter centered at $0.935 \mu\text{m}$. These observations by Venus Express are obviously crucial to investigate the large-scale circulation in the deep atmosphere, the meteorology of H₂SO₄ clouds, and to search for possible volcanic activity. The latter can be sought through images of the surface at $1.0 \mu\text{m}$ on the night side (looking for hot spots) or spectroscopic monitoring in the nightside windows (looking for local enhancement of specific gases such as SO₂).

[29] The nightside windows are clearly an important target for the Venus Express mission. However, the absolute preci-

sion with which the absorbers' abundances can be retrieved from these observations is still limited by uncertainties in the modeling of the CO₂ opacity. A continuum absorption, due to the far wings of the strong CO₂ bands outside the windows and to collision-induced bands, limits the depth of the levels contributing to the emission. Up to now this opacity has been reliably measured only in the 2.3-micron window and at room temperature [*Tonkov et al.*, 1996]. Measurements in other windows and in conditions relevant to Venus' deep atmosphere are urgently needed. Analysis of the nightside emission would also benefit from improved molecular line-lists especially for CO₂ and to a lesser extent H₂O. The high-temperature CO₂ database (HITEMP) used up to now [*Pollack et al.*, 1993] allows a correct reproduction of the CO₂ bands present in the observed windows but significant discrepancies clearly remain.

[30] Other quantities important for the sulfur cycle will require in situ measurements by future missions. Of particular importance is the determination of the abundances of gases such as CO, SO₂, OCS, S₂ or H₂S *near the surface* to constrain the oxidation state of the lower atmosphere and surface, and determine the stability of various minerals. Measurements at higher altitudes of, e.g., SO₃, SO or elemental sulfur are also needed to better understand the sulfur cycle and the chemistry at work below the cloud base.

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